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CONDITIONING OF FLY ASH WITH SULFUR TRIOXIDE AND AMMONIA

Edward B. Dismukes

Southern Research Institute

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The report summarizes research on the conditioning of fly ash in coal-burning electric power stations with two flue-gas additives--sulfur trioxide and ammonia. It presents experimental data on the use of these additives to improve the efficiency of electrostatic precipitation of fly ash by adjusting the electrical resistivity of the ash and by other less widely recognized mechanisms. The report shows that the primary role of sulfur trioxide is lowering resistivity from the excessive values found with ash from low-sulfur coals. It also indicates that the role of ammonia does not involve a change in resistivity, despite findings to the contrary by other investigators. At least for the specific circumstances investigated, the research data indicate that conditioning by ammonia involves a space-charge enhancement of the electric field in the interelectrode space of a precipitator and, sometimes additionally, an increase in the cohesiveness of the collected ash. The report addresses both the theoretical aspects of conditioning mechanisms, and such practical matters as the effectiveness of each agent as a function of the concentration added, the facilities used for adding the agent, the chemical composition of the ash treated, and the temperature of the ash during conditioning and precipitation.

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Abstract

This report summarizes research on the conditioning of fly ash in coal-burning electric power stations with two flue-gas additives—sulfur trioxide and ammonia. It presents experimental information regarding the use of these additives to improve the efficiency of electrostatic precipitation of fly ash by adjustment in the electrical resistivity of the ash and by other mechanisms less widely recognized than resistivity modification. The report shows that the primary role of sulfur trioxide is lowering resistivity from the excessive values found with ash from low-sulfur coals. It indicates that the role of ammonia, to the contrary, does not involve a change in resistivity, despite findings to the contrary by other investigators. At least for the specific circumstances investigated, the research data indicate that conditioning by ammonia involves a space-charge enhancement of the electric field in the interelectrode space of a precipitator and, sometimes additionally, an increase in the cohesiveness of the collected ash. The report not only addresses the theoretical aspects of conditioning mechanisms but deals with such practical matters as the effectiveness of each agent as a function of the concentration added, the facilities used for adding the agent, the chemical composition of the ash treated, and the temperature of the ash during conditioning and precipitation.

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CONTENTS

Page

Abstract iii

List of Figures vi

List of Tables viii

Acknowledgments xii

Sections

I Conclusions 1

II Recommendations 4

III Introduction 7

IV General Description of Research on Conditioning by Sulfur Trioxide and Ammonia 15

V Results of Studies of Conditioning with Sulfur Trioxide 20

VI Results of Studies of Conditioning with Ammonia 70

VII Discussion of Conditioning with Sulfur Trioxide 116

VIII Discussion of Conditioning with Ammonia 135

IX References 143

X Appendix. Experimental Methods 148

FIGURES

No. Page

1. Electrical Resistivity of Fly Ash at Kingston Unit 5 22

2. Concentrations of Sulfur Trioxide at Kingston Unit 5 23

3. Chemical Properties of Fly Ash at Kingston Unit 5 25

4. Schematic Diagram of Electrical Sections in Collector 1B at the Bull Run Plant 51

5. Current Density *Versus* Voltage in Collector 1B of the Bull Run Plant (August 1972) 53

6. Concentration of Sulfur Trioxide as a Function of Gas Temperature at the Bull Run Plant (July 1974) 65

7. Current Density *Versus* Voltage in Collector 1B of the Bull Run Plant (July 1974) 68

8. Schematic Diagram of Electrical Sections in Collector 7A at the Widows Creek Plant 77

9. Current Density *Versus* Voltage in Collector 7A of the Widows Creek Plant (Low-Sulfur Coal, June 1972) 79

10. Current Density *Versus* Voltage in Collector 7B of the Widows Creek Plant (Low-Sulfur Coal, July 1972) 81

11. Current Density *Versus* Voltage in Collector 1C of the Bull Run Plant (Ammonia Conditioning, September 1972) 88

12. Current Density *Versus* Voltage in Collector 1C of the Bull Run Plant (Ammonia Conditioning, October 1972) 89

13. Current Density *Versus* Voltage in Collector 7A of the Widows Creek Plant (High-Sulfur Coal, November 1972) 98

No. Page

14. Rapidity of the Effect of Ammonia Injection on the Voltage Supplied to the Inlet Electrical Field of Gallatin Precipitator 4C 108

15. Current Density *Versus* Voltage in Precipitator 4C of the Gallatin Plant 109

16. Effects of Changes in Ammonia Injection on the Emission of Particulate from Gallatin Precipitator 4C as Indicated by the Bailey Bolometer (20 ppm of NH_3) 111

17. Effects of Changes in Ammonia Injection and Electrode Rapping on the Emission of Particulate from Gallatin Precipitator 4C as Indicated by the Bailey Bolometer (20 ppm of NH_3) 113

18. Resistivity as a Function of the Concentration of Injected Sulfur Trioxide 120

19. Resistivity as a Function of the Sulfate Concentration in Fly Ash 122

20. Dew Points of Vapor Mixtures of Sulfur Trioxide and Water 125

21. Resistivity Apparatus Using a Mechanical Cyclone Dust Collector (Cohen and Dickinson[26]) 149

22. Cyclone Probe Inserted in Duct (Nichols[27]) 151

23. Point-to-Plane Resistivity Probe Equipped for Thickness Measurement (Nichols[27]) 152

TABLES

No.		Page
1.	Power Plants Investigated During the Research on the Conditioning of Fly Ash	19
2.	Composition of Fly Ash from the Kingston Plant	26
3.	Electrical Resistivity of Fly Ash at Cherokee Unit 2	28
4.	Concentrations of Flue Gases at Cherokee Unit 2	29
5.	Chemical Properties of Fly Ash at Cherokee Unit 2	29
6.	Composition of Fly Ash from the Cherokee Plant	31
7.	Electrical Resistivity and Sulfate Content of Fly Ash at Plant 3	32
8.	Composition of Fly Ash from Plant 3	32
9.	Electrical Resistivity of Fly Ash at Cherokee Unit 3	35
10.	Concentrations of Flue Gases at Cherokee Unit 3	36
11.	Chemical Properties of Fly Ash at Cherokee Unit 3	36
12.	Composition of Fly Ash from Arapahoe Unit 4	39
13.	Electrical Resistivity of Fly Ash at Arapahoe Unit 4	39
14.	Concentrations of Flue Gases at Arapahoe Unit 4	39
15.	Chemical Properties of Fly Ash at Arapahoe Unit 4	40
16.	Composition of Fly Ash from Plant 6	41
17.	Electrical Resistivity of Fly Ash at Plant 6	43
18.	Concentrations of Flue Gases at Plant 6	44
19.	Chemical Properties of Fly Ash at Plant 6	44

No. Page

20. Composition of Fly Ash from the Bull Run Plant (August 1972) 46

21. Electrical Resistivity of Fly Ash at the Bull Run Plant (August 1972) 47

22. Chemical Properties of Fly Ash at the Bull Run Plant (August 1972) 48

23. Concentrations of Flue Gases at the Bull Run Plant (August 1972) 49

24. Precipitator Electrical Data from the Bull Run Plant (August 1972) 52

25. Composition of Fly Ash from the Bull Run Plant (July 1974) 56

26. Precipitator Efficiencies at the Bull Run Plant (July 1974) 57

27. Precipitation Efficiency as a Function of Gas Temperature at the Bull Run Plant (July 1974) 58

28. Electrical Resistivity of Fly Ash at the Bull Run Plant (July 1974) 59

29. Chemical Properties of Individual Samples of Fly Ash Collected in Thimbles at the Bull Run Plant (July 1974) 60

30. Chemical Properties of Composite Samples of Fly Ash Collected in Thimbles at the Bull Run Plant (July 1974) 61

31. Chemical Properties of Composite Samples of Fly Ash from Precipitator Hoppers at the Bull Run Plant (July 1974) 62

32. Concentrations of Sulfur Trioxide Equivalent to the Concentrations of Sulfate in Fly Ash at the Bull Run Plant (July 1974) 63

33. Precipitator Electrical Data from the Bull Run Plant (July 1974) 67

34. Composition of Fly Ash from a Low-Sulfur Coal at Widows Creek Unit 7 (June-July 1972) 72

No. Page

35. Electrical Resistivity of Fly Ash from a Low-Sulfur Coal at Widows Creek Unit 7 (June-July 1972) 74

36. Chemical Properties of Fly Ash from a Low-Sulfur Coal at Widows Creek Unit 7 (July 1972) 74

37. Concentrations of Flue Gases from a Low-Sulfur Coal at Widows Creek Unit 7 (June-July 1972) 75

38. Peak Values of Precipitator Secondary Voltages and Secondary Currents at Widows Creek Unit 7 (Low-Sulfur Coal, July 1972) 80

39. Primary Voltages and Currents Supplied by the Transformer-Rectifier Sets at Widows Creek Unit 7 (Low-Sulfur Coal, July 1972) 80

40. Compositions of Fly Ash from the Bull Run Plant (Ammonia Conditioning, September-October 1972) 83

41. Electrical Resistivity of Fly Ash at the Bull Run Plant (Ammonia Conditioning, September 1972) 84

42. Chemical Properties of Fly Ash at the Bull Run Plant (Ammonia Conditioning, October 1972) 85

43. Concentrations of Flue Gases at the Bull Run Plant (Ammonia Conditioning, September 1972) 86

44. Precipitator Electrical Data from the Bull Run Plant (Ammonia Conditioning, September 1972) 87

45. Concentrations of Submicron Particles at the Bull Run Plant (Ammonia Conditioning, October 1972) 91

46. Composition of Fly Ash from a High-Sulfur Coal at Widows Creek Unit 7 (November 1972) 93

47. Precipitator Efficiencies with High-Sulfur Coal at Widows Creek Unit 7 (June-July 1970) 94

48. Electrical Resistivity of Fly Ash from a High-Sulfur Coal at Widows Creek Unit 7 (November 1972) 95

49. Chemical Properties of Fly Ash from a High-Sulfur Coal at Widows Creek Unit 7 (November 1972) 95

50. Concentrations of Flue Gases from a High-Sulfur Coal at Widows Creek Unit 7 (November 1972) 96

No. Page

51. Precipitator Electrical Data from Widows Creek Unit 7 (High-Sulfur Coal, November 1972) 97

52. Concentrations of Submicron Particles at the Widows Creek Plant (High-Sulfur Coal, November 1972) 99

53. Composition of Fly Ash from Gallatin Unit 4 101

54. Fly-Ash Emission from Gallatin Unit 4 (Collector 4C) 102

55. Emission of Fly Ash in Various Size Ranges at Gallatin Unit 4 (Collector 4C) 103

56. Electrical Resistivity of Fly Ash at Gallatin Unit 4 105

57. Chemical Properties of Fly Ash at Gallatin Unit 4 106

58. Concentrations of Flue Gases at Gallatin Unit 4 106

59. Precipitator Electrical Data from Gallagin Unit 4 107

60. Concentrations of Submicron Particles at Gallatin Unit 4 107

61. Emission of Fly Ash in Various Size Ranges as a Function of Electrode Rapping and Ammonia Injection at Gallatin Unit 4 114

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SECTION I

CONCLUSIONS

The use of gaseous chemical compounds as "conditioning" agents for fly ash is an effective way to improve the electrostatic precipitation of the particulate produced in a coal-burning power plant. The value of this technology has been long recognized. Certain aspects of conditioning with sulfur trioxide and ammonia, however, are clarified by the research described in this report: (1) the circumstances under which conditioning is effective and (2) the mechanisms by which conditioning can occur (which include processes other than the most widely known process of lowering the electrical resistivity of the ash).

CONDITIONING WITH SULFUR TRIOXIDE

Practical Considerations

The most significant function of sulfur trioxide conditioning is to lower the resistivity of fly ash from low-sulfur coals. In regard to this process, the principal conclusions from this research are as follows:

- The various types of injection systems investigated produce equally effective results when properly engineered and maintained. (These systems are based on anhydrous sulfur trioxide, concentrated sulfuric acid, and catalytically oxidized sulfur dioxide as source materials.)

- Satisfactory sites of injection include the flue-gas ducts in locations upstream from a precipitator, upstream from the combination of a precipitator and a mechanical collector, and between the two types of collectors.

- The minimum required concentration of sulfur trioxide is in the range from 5 to 20 ppm, with the appropriate value depending upon the flue-gas temperature and the fly-ash composition.

- Fly ash of widely varying compositions can be successfully conditioned with sulfur trioxide. The main effect of compositional variations is the requirement of more conditioning agent with high-alkalinity ash.

- Fly ash can be successfully conditioned at temperatures ranging from 110°C to at least 160°C and perhaps near 200°C.

One of the secondary functions of sulfuric trioxide conditioning is to increase the cohesiveness of fly-ash particles and minimize rapping reentrainment. This role of the conditioning agent is to be expected if the resistivity of the ash is not high enough to maintain an electric force as an adequate restraint against reentrainment.

Theoretical Factors

Lowering the resistivity of fly ash obviously occurs with sulfur trioxide conditioning. The process involves the codeposition of the injected sulfur trioxide and the naturally occurring water vapor from the flue gas onto the surfaces of ash particles. Either adsorption or condensation of the two gases leads to increased surface conduction. The mechanism of conduction on conditioned ash may involve hydrogen ion migration in a surface film of sulfuric acid or acid-induced mobility of alkali metal ions normally present in the ash.

Other mechanisms of conditioning apparently include a change in the cohesiveness of fly ash, as mentioned above, and a space-charge effect. The first of these mechanisms involves a modification of the ash surface properties, as does the lowering of resistivity. The second mechanism involves a change in the electrical properties of the flue gas rather than the fly ash.

CONDITIONING WITH AMMONIA

Practical Considerations

The utility of ammonia as a conditioning agent may be more restricted than that of sulfur trioxide. The use of ammonia conditioning to overcome the prevalent problem of high resistivity of fly ash from low-sulfur coals, especially those of

Western origin, cannot be recommended on the basis of the direct results of this research. However, the utility of ammonia conditioning under these circumstances was not investigated during this program and needs clarification by further research.

The value of ammonia as a conditioning agent was established clearly with fly ash from selected coals of Eastern origin having both low- and high-sulfur contents. With these fuels, the resistivity of the fly ash was not excessive, but ammonia injection was able to improve collection efficiency through mechanisms involving a space-charge effect in the flue gas and an increase in the cohesiveness of the ash.

Theoretical Factors

In connection with the mechanisms of ammonia conditioning, this research led to the following conclusions:

- Ammonia has little if any effect on the resistivity of fly ash under the specific power-plant conditions investigated. However, this conclusion does not necessarily mean that the effect of ammonia on resistivity will always be negligible.

- Ammonia conditioning occurs through a space-charge mechanism, through which the electric field in the flue-gas stream between precipitator corona wires and collection electrodes is enhanced. Reaction of ammonia with naturally occurring sulfur trioxide and water vapor to produce fine particles of ammonium sulfate or bisulfate is evidently the first step in this mechanism. Electrical charging of the particulate and reduction of the average mobility of charge carriers evidently occurs subsequently and serves as the direct cause of the field enhancement.

- Ammonia conditioning of fly ash of abnormally low resistivity appears to include an increase in the cohesiveness of the ash with an attendant reduction in rapping reentrainment.

SECTION II

RECOMMENDATIONS

The preceding discussion of the conclusions from this research includes at least some indirect recommendations on conditioning with sulfur trioxide and ammonia that are based on present knowledge. The following discussion offers explicit recommendations on additional research that is needed.

USE OF SULFUR TRIOXIDE

One of the major needs in the power industry is the ability to predict the electrical resistivity of fly ash to be produced by fuel from a new coal field and, thus, to predict the need for conditioning or an alternative method of overcoming high resistivity. This need can only be satisfied if relationships are established involving the composition of representative core samples of coal, the composition of the fly ash and the flue gas to be produced by the coal, and the susceptibility of the ash to conditioning by normal constituents of the flue gas and by added sulfur trioxide.

Fundamental laboratory work is recommended to provide the information required for predicting fly-ash resistivity with and without added sulfur trioxide as a conditioning agent. Preliminary research of this nature has already been initiated at Southern Research Institute with the support of the Environmental Protection Agency. This research should be continued with attention directed to these specific questions:

(1) What is the relationship of the composition of fly ash to the composition of the mineral constituents of coal?

(2) How is the susceptibility of fly ash to conditioning by water vapor and sulfur trioxide related to the chemical composition of fly ash and the nature of the gaseous environment?

(3) What are the mechanisms of surface conduction on conditioned fly ash of varying compositions?

A practical benefit from the fundamental studies described above will be guidance in determining the range of circumstances under which sulfur trioxide will be beneficial. Information on this matter is already available from the power-plant studies described in this report. However, an extension of this information will permit greater confidence in the results to be achieved with sulfur trioxide conditioning in full-scale practice.

Two practical questions deserve attention. One is how to optimize the design of an injection manifold for sulfur trioxide and gain maximum utilization of the agent. A fundamental problem in injecting sulfur trioxide is to avoid acid condensation at the interface between the concentrated vapor being injected and the flue gas serving as a diluent. Another question is to determine the merits of injecting sulfur trioxide upstream from the air preheater. A potential advantage of injecting the agent at this location is to eliminate the possibility of condensation at the interface of the injected agent and the flue gas.

Another practical matter is to assess the impact of sulfur trioxide conditioning on the emission of sulfate-containing particulates from a power plant. If all of the injected sulfur trioxide is collected by the ash, no increase in sulfate emission occurs. It is evident, however, that sometimes part of the sulfur trioxide enters the stack as a vapor and that it is able to condense as sulfuric acid mist in the plume leaving the stack. The magnitude of sulfate loss and the circumstances that control this effect need to be ascertained.

USE OF AMMONIA

A major potential application of ammonia conditioning—treatment of high-resistivity fly ash from low-sulfur Western coals—has not been realized. It does not appear that sufficient research to determine the value of ammonia conditioning in this respect has yet been attempted. It is certainly desirable to resolve the question of whether ammonia can control the problem of high resistivity, however, for the use of this agent would be less costly, less hazardous, and more convenient than the use of sulfur trioxide.

Two approaches are recommended to assess the value of ammonia as a substitute for sulfur trioxide in treating high-resistivity fly ash:

(1) Analyze in detail the results of investigations of ammonia conditioning in Australia and the Soviet Union and attempt to deduce the probable effect of this process on ash of interest in the United States.

(2) Include studies of the fundamental aspects of ammonia conditioning in the previously described laboratory studies of sulfur trioxide conditioning.

If the results of these two approaches warrant further studies of ammonia conditioning, a program to conduct such studies in a pilot-plant or full-scale precipitator should be initiated.

A possible effective mechanism of ammonia conditioning in a precipitator collecting high-resistivity ash is the suppression of the electrical manifestations of back corona without necessarily lowering resistivity. Perhaps some type of space-charge effect is able to suppress the massive flow of positive ions that occurs from regions of back corona to the discharge electrodes in a precipitator, thus increasing the effective operating voltage. For practical as well as fundamental reasons, research to clarify the effect of ammonia on back corona needs to be undertaken.

A final practical question that needs attention is whether the space-charge effect encountered with ammonia conditioning leads to an unacceptable increase in the emission of fine particulate from a power station. This question was considered during the research described in this report, but it was not fully resolved and it needs further consideration.

SECTION III

INTRODUCTION

Fly ash emitted from coal-burning electric power stations is one of the most important causes of air pollution in an industrialized community. This particulate matter may be removed from the effluent gas of a power boiler by several approaches based on high-efficiency electrostatic precipitators, liquid scrubbers, and fabric filters. For many years, collection of fly ash in electrostatic precipitators has been the most commonly used method for cleaning gas from power boilers. Even today, the supremacy of electrostatic precipitators for gas cleaning in the power industry continues. However, there are increasingly stringent requirements for particulate control, especially the material of small size. Thus, achieving the needed efficiency of electrostatic precipitators requires elimination of unfavorable dust properties wherever possible, such as the reduction of excessively high electrical resistivity.

EFFECT OF THE ELECTRICAL RESISTIVITY OF FLY ASH ON THE PERFORMANCE OF AN ELECTROSTATIC PRECIPITATOR

For the efficient removal of fly ash from flue gases in an electrostatic precipitator, several conditons must be satisfied. One of the most important conditions is that the electrical resistivity of the ash deposited on the collector electrodes shall lie within an appropriate range of values, somewhat difficult to define but described by some authors as having a lower limit of about 1×10^7 to 1×10^9 ohm cm and an upper limit of about 1×10^{10} ohm cm.[1-3] Other conditions, however, are of comparable importance and must be satisfied simultaneously. For example, the gas flow distribution in the precipitator must be reasonably uniform, the velocity of the gas passing between the corona wires and the collector electrodes must not be excessive, and the power supplies must be capable of maintaining an adequate current density at the electrodes.

If the resistivity of the collected ash is too low, only a small voltage drop can be maintained across the collected layer. Hence, the electrical force holding the ash to the collector electrodes may be so low that reentrainment of ash particles in the adjacent gas stream becomes severe. On the other hand, if the resistivity of the collected ash is too high, either of the following phenomena may occur:

(1) The resistance through the collected layer of ash will lower the corona current that can be produced with the normal operating voltage and, as a consequence, the electric field in the gas stream and the resulting migration velocities of negatively-charged fly-ash particles toward the collecting electrodes will be markedly reduced. Usually, an attempt to overcome the effect of excessive resistance through the collected ash with increased voltage and correspondingly increased electric field will meet with failure as the result of rapid sparking.

(2) The resistance through the collected layer of ash may be sufficient to cause electrical breakdown in the layer with attendant formation of positive gaseous ions ("back corona" or "reverse ionization"), neutralization of negative charges on the ash particles, and reentrainment of the ash particles in the gas stream.

Judging from the published literature, problems stemming from low resistivity are rare, but those stemming from high resistivity are fairly common, especially in power plants burning low-sulfur coals. High resistivity of ash from low-sulfur coal is attributed to the low concentration of sulfur trioxide that is produced in the combustion process and the resulting failure of the ash to collect sufficient amounts of sulfur trioxide and water vapor from the gas stream to produce a conductive film on the particle surfaces. Owing to the increasing emphasis on the use of low-sulfur coals to minimize emission of sulfur oxides and the simultaneous demands for improvements in fly-ash collection, increasing efforts are being made in the power industry to find methods to overcome the problem of high resistivity.

CONTROL OF ELECTRICAL RESISTIVITY PROBLEMS IN ELECTROSTATIC PRECIPITATORS

There are, at present, essentially four methods of overcoming the problem of high resistivity of fly ash:

(1) Operate the electrostatic precipitator at temperatures well below the normal range (e.g., around 120°C), at which enhanced collection of water vapor can produce a sufficiently conductive surface film to make up for the shortage in sulfur trioxide.

(2) Operate a so-called "hot precipitator" ahead of the air preheater with temperature in excess of 300°C, where the volume conductivity of fly ash (in contrast to the surface conductivity referred to above) is high enough to permit efficient precipitation.

(3) Operate a precipitator at customary temperatures (around 150°C) and inject a chemical conditioning agent in the flue gas to make up for the shortage of naturally produced sulfur trioxide.

(4) Increase substantially the specific collecting area of the precipitator electrodes (the ratio of the total electrode area to the volume flow rate of flue gas).

The best known chemical conditioning agents are sulfur trioxide (SO_3) and ammonia (NH_3). Both of these compounds have been in use for many years; even so, the circumstances under which these compounds are most effective and the mechanisms by which they act (ammonia, especially) are not fully understood.[2,3] Other conditioning agents that are in use at present or that are potentially useful include sulfamic acid, ammonium sulfate, and ammonium bisulfate. The mechanisms of action of these compounds is even more uncertain than those of sulfur trioxide and ammonia.[4]

Although the problem of low resistivity is less common than the problem of high resistivity, power plants burning high-sulfur coals and producing high concentrations of sulfur trioxide are subject to this difficulty. There have been at least two technical papers recognizing low resistivity as a source of difficulty and reporting success in the use of ammonia as a flue-gas additive to overcome the problem.[5,6]

CONDITIONING OF FLY ASH WITH SULFUR TRIOXIDE

In this report as in publications by other investigators, conditioning of fly ash with sulfur trioxide refers not only to the use of this compound (SO_3) but also to the alternative use of the chemically equivalent compound sulfuric acid (H_2SO_4). Injection of the vapor of either compound into a stream of flue gas at customary precipitator temperatures of about 150°C leads to the conditioning of fly ash only by sulfuric acid, for sulfur trioxide is quantitatively converted to the acid by reaction with water vapor. Even though sulfur trioxide is frequently spoken of as one of the components of flue gas, it only occurs as this substance at temperatures in the gas train above 300°C. As the temperature falls to values below 300°C downstream from the air preheater, the normally occurring sulfur trioxide is converted to sulfuric acid. Likewise, in the lower range of temperatures, injected sulfur trioxide is converted to the acid. (Thermodynamic data supporting the foregoing statements about the conversion of sulfur trioxide to sulfuric acid have been published in the JANAF Tables.[7])

Sulfur trioxide has been recognized for many years as a useful conditioning agent for various dusts with high electrical resistivity. Some of the earliest and most important experimental work on conditioning with sulfur trioxide was conducted by Chittum;[8] later significant work was carried out by White.[1] This experimentation was done largely on a laboratory scale, but it has nevertheless proved valuable in understanding processes of conditioning in full-scale precipitators.

Sulfur trioxide was one of a long series of conditioning agents investigated by Chittum between 1942 and 1945 at the Western Precipitation Corporation (now a division of Joy Manufacturing Company).[8] Chittum demonstrated the relative efficiencies of different conditioning agents for various types of dusts in a "racetrack" apparatus, in which the dust and conditioning agent were recirculated in an airstream and precipitated in a point-plane device that permitted determination of resistivity. Chittum found that in conditioning basic dusts (such as magnesium oxide), sulfur trioxide and other acidic compounds were the most effective conditioning agents. He found on the other hand that in conditioning acidic dusts (such as boric acid), ammonia and other basic compounds were most effective. He concluded that the conditioning agent activated the adsorption of water vapor to provide a conductive surface layer on the suspended particles and that the activation process was favored by the use of conditioning agents that opposed the dust in acid-base character.

Chittum apparently was not directly concerned about the conditioning of fly ash; his main concern in a practical sense was the conditioning of catalyst dust in the petroleum refining industry. White, on the other hand, was concerned directly with the conditioning of fly ash.[1] He demonstrated, for example, the interrelationship between the vapors of water and sulfur trioxide in conditioning fly ash and the importance of flue-gas temperature in determining the concentration of sulfur trioxide needed for efficient conditioning. Like Chittum, White was concerned with the mechanism of conditioning, not just the practical results in terms of precipitation efficiency. Thus, White's experimental work included determinations of the electrical resistivity of fly ash before and after treatment with the conditioning agent.

During the decade between 1960 and 1970, practical interest in sulfur trioxide as a conditioning agent for fly ash accelerated. With increased use of low-sulfur coals in the utility industry, some means of overcoming the attendant loss of precipitator performance became necessary. As indicated previously in this report, chemical conditioning of the fly ash was one of the practical solutions investigated. Some of the earliest practical steps toward developing the use of sulfur trioxide as a flue-gas additive were taken by Lodge-Cottrell, Ltd., in Great Britain. Various papers published by representatives of this firm described the practical value of sulfur trioxide injection and showed the expected effect of lowered fly-ash resistivity on the basis of field or *in situ* measurements of this parameter.[9,10] Other papers published within the same span of time described the practical value of sulfur trioxide injection without clarifying the mode of action.[11,13]

All efforts to overcome the problem of high-resistivity fly ash with the injection of sulfur trioxide have not been successful. Baxter[6] and Watson and Blecher[14] described failures of sulfur trioxide to produce the expected improvement in precipitation efficiency, even when the level of injection was far higher than the normal level (producing about 10 to 20 ppm by volume of sulfur trioxide after dilution with flue gas). Baxter's paper states that sulfur trioxide failed to act as desired at one power plant, even when the level of injection was high enough to intensify the plume of particulate emitted to the atmosphere (presumably the result of the formation of a mist of condensed sulfuric acid). The unsuccessful trials of sulfur trioxide conditioning have no simple explanation. One factor that must be kept in mind, however, is that a conditioning agent may eliminate the problem of high resistivity without having any effect on other problems such as inadequate precipitator size or poor gas distribution in the precipitator.

Anomalous results from sulfur trioxide conditioning have been obtained in some instances where high resistivity may not have been the basic cause of poor precipitator performance. The experimental work of Dalmon and Tidy[15,16] offers a possible explanation for some of these results. These investigators found that the efficiency of precipitation of low-resistivity ash containing a high percentage of unburned carbon could be improved by using sulfur trioxide as a binder for the individual particles of ash and carbon. They concluded that increased cohesiveness of the fly ash and carbon deposited on precipitator electrodes could overcome excessive reentrainment as the factor limiting precipitator performance.

CONDITIONING OF FLY ASH WITH AMMONIA

The value of ammonia as a conditioning agent was first reported in 1942, in an electrostatic precipitator for recovering catalyst dust in petroleum refining.[3] The use of ammonia and related compounds (organic amines) for improving the precipitation of catalyst dust then became part of the intensive study undertaken by Chittum at the Western Precipitation Corporation between 1942 and 1945. The catalyst dust was a mixture of silicates of various metals and was acidic in its behavior, producing a pH of less than 7 in a slurry with water. Chittum found that ammonia and amines were much more effective than sulfur trioxide and other acids in lowering the resistivity of the catalyst dust. Chittum's finding, of course, was consistent with his conclusion that the best conditioning agent is one that opposes the dust in acid-base character.

Usually, the concentrations of dusts and conditioning agents in Chittum's laboratory experiments were quite high. Calculations of the concentration based on the total volume of his racetrack apparatus and the total amounts of catalyst dust and ammonia added lead to dust concentrations as high as 2,300 g/m^3 (1,000 gr/ft^3) and ammonia concentrations as high as 10,000 ppm by volume. Undoubtedly, the additions of dust and conditioning agent were made gradually; thus, instantaneous concentrations probably were never as high as the values cited, but they must have greatly exceeded the concentrations of fly ash and conditioning agents that are found in power-plant effluents. It is true that Chittum's relative concentrations of dust and conditioning agent corresponded roughly to the relative concentrations of fly ash and conditioning agents that are common in power-plant effluents; however, it is likely that the high absolute concentration of ammonia in Chittum's experiments may have been a critical factor in the adsorption of ammonia on the surface of the catalyst particles and the resulting lowering of electrical resistivity.

Generally, the volatility of a gas can be roughly correlated with the ease of adsorption of the gas on a solid. Ammonia is highly volatile, having a boiling point of -33°C, and its adsorption on alumina-silica catalysts at elevated temperatures requires high partial pressures of the gas.[17] Thus, adsorption of ammonia on fly ash, which is somewhat similar in composition to Chittum's alumina-silica catalysts, appears unlikely at concentrations of the order of 15 to 20 ppm in flue gas at temperatures around 150°C. Adsorption of ammonia on fly ash may be greatly aided if the surface of the ash is acidic; however, the occurrence of an acidic surface material is probably the result of the adsorption of sulfur trioxide, and the resistivity of the ash should not in that event be unacceptably high.

Although it is difficult to visualize the adsorption of ammonia as effective in conditioning a high-resistivity fly ash, there have been occasions when it may have occurred. Baxter reported success in conditioning high-resistivity fly ash in several power plants.[6] In each plant, the injection of 15 ppm of ammonia lowered the emission of fly ash from the precipitator, increased the precipitator power consumption, lowered the resistivity of the fly ash (measured under laboratory conditions), and lowered the acidity of the ash. Watson and Blecher reported that the injection of 15 to 20 ppm of ammonia improved the efficiency of collection of an acidic ash;[14] these investigators also reported voltage-current data for their precipitator indicating that ammonia suppressed the occurrence of back corona, a phenomenon sometimes caused by high resistivity. Other investigators whose work has not been published have reported results of precipitator tests indicating that ammonia lowered fly-ash resistivity.[18-20]

In contrast to the reports indicating that ammonia conditioning lowered fly-ash resistivity from excessive values, other reports have indicated that ammonia conditioning increased the resistivity of fly ash when the value was too low. One instance of this phenomenon was reported by Baxter,[6] who found that 15 ppm of ammonia produced an increase in resistivity (from 5×10^8 to 1×10^{10} ohm cm by laboratory measurement), a decrease in the acidity of the ash, and accompanying increases in precipitator power consumption and efficiency. Another apparent instance of increased resistivity was described by Reese and Greco.[5] These authors discussed a power plant burning high-sulfur coal and collecting fly ash at a precipitator temperature of about 130°C. (This plant, Widows Creek Station in the TVA system, is discussed later in the section of this report covering experimental work.) The authors were able to reach acceptable precipitator efficiencies by either of two methods: (1) raising the gas temperature to 155°C or (2) injecting ammonia at a concentration of about 15 ppm with no temperature change. The authors' assumption was that either method increased the resistivity of the fly ash (by lowering the amount of sulfuric acid vapor condensed on the surface of the ash) and thus decreased reentrainment of fly ash in the precipitator.

In a significant fundamental study of various conditioning agents for fly ash, Dalmon and Tidy compared ammonia and various other compounds for conditioning fly ash that was highly basic in character[16] (in opposition to the acidic fly ash treated by Baxter[6] and by Watson and Blecher[14]). Dalmon and Tidy burned a low-sulfur paraffin oil in the laboratory to produce a gas stream essentially free of sulfur oxides and added the fly ash and each of the conditioning agents to this gas stream before it entered a small electrostatic precipitator. They found that ammonia produced a slight increase in the efficiency of the precipitator without producing a measurable change in the resistivity of the ash; they then posed this question:[21] "Could the small quantities used be influencing the voltage-current characteristic to enable a high working voltage?"

Dalmon and Tidy also found that if sulfur dioxide was added to the gas stream to simulate the actual concentration produced by a low-sulfur coal, the effects of ammonia injection were inconsequential unless hydrogen chloride was added also (this gaseous compound is present in flue gas at varying concentrations depending upon the amounts of chloride salts that are present in the coal). The authors attributed the relationship involving ammonia and hydrogen chloride to the formation of small gas-borne solid particles of ammonium chloride, the coprecipitation of this material with the fly ash, and the resultant lowering of the resistivity of the ash. Ammonium ion was usually not found in ash analyses, but chloride ion was found. Loss of ammonium ion was attributed to the reaction of this ion with the basic constituents of the ash and the release of ammonia to the gas stream. Hence, the authors concluded that the effect of ammonia in the presence of hydrogen chloride was to aid the uptake of chloride ion by the ash.

It is reasonable to expect that the combination of ammonia, sulfur trioxide, and water vapor could produce particles of ammonium bisulfate or ammonium sulfate and condition fly ash by a mechanism analogous to the one described by Dalmon and Tidy. It is reasonable to propose as an alternative that the electrical charging of the particles of either ammonium salt could increase the electric field in the precipitator and effectively "condition" the ash through a space-charge effect. Experimental evidence for the latter mechanism of action by ammonia is discussed at length in the sections of this report dealing with experimental work.

SECTION IV

GENERAL DESCRIPTION OF RESEARCH ON CONDITIONING BY SULFUR TRIOXIDE AND AMMONIA

Experimental studies of conditioning of fly ash with sulfur trioxide and ammonia were carried out by Southern Research Institute during 1970-1971 under Contract CPA 70-149 with the Environmental Protection Agency[22] and during 1972-1974 under Research Agreement TV36921A with the Tennessee Valley Authority.[23] Most of the work for EPA was concerned with sulfur trioxide as the conditioning agent; but the studies included a limited investigation of ammonia conditioning. The later work supported by TVA included an extension of the studies of sulfur trioxide conditioning; however, it consisted primarily of efforts to resolve questions about ammonia conditioning that were not answered during the first investigation.

OBJECTIVES OF THE RESEARCH

During 1970, the existence or planned installation of facilities for injecting sulfur trioxide in various power plants in the United States created the opportunity for Southern Research Institute to investigate the effectiveness of this conditioning agent in overcoming problems caused by high-resistivity fly ash from domestic coals. One of the most ambitious programs of installing sulfur trioxide conditioning facilities was undertaken by the Public Service Company of Colorado, which has now installed such facilities for eight power units in three plants.[24,25] Before the negotiations for a research contract between the Institute and the Environmental Protection Agency were completed, an agreement between the Institute and the Public Service Company had been reached to permit members of the Institute staff to conduct research at the power plants to be equipped with conditioning facilities.

The objective of the planned program of research with such sulfur trioxide facilities that might become available (including others as well as those in Colorado) was to investigate the role of each of the following in determining the effectiveness of conditioning: (1) coal composition, (2) fly-ash composition, (3) flue-gas composition and temperature, (4) concentration of sulfur trioxide injected, (5) source of the sulfur trioxide injected, and (6) location of the point of sulfur trioxide injection in the flue-gas train. The results of the investigation were expected to provide general, practical guidelines of value to utility companies which might need to predict the value of chemical conditioning in power plants encountering the problem of high-resistivity fly ash. The results of the investigation were also expected to shed light on some theoretical aspects of the conditioning process that were not clearly understood.

The key to the experimental approach was to make in situ measurements of the electrical resistivity of fly ash with and without conditioning. Changes in resistivity as a result of conditioning but not changes in precipitator performance were to be measured. The rationale for this approach was to focus attention on the specific process by which improved efficiency could be expected, assuming that no other problem was important in controlling the efficiency. No effort was made to diagnose causes of poor precipitator performances other than high-resistivity fly ash.

Experience with various devices for measuring resistivity proved to be necessary before acceptable measurements could be made. An apparatus of the cyclone type that was developed by Cohen and Dickinson[26] and used in investigations by Lodge-Cottrell, Ltd.,[9,10] was used briefly but then discarded because of its lack of reliability. Another cyclone device and a point-plant apparatus were then developed and found to be more satisfactory in their performance. Descriptions of these two resistivity probes have been given by Nichols of Southern Research Institute in another report.[27] A brief discussion of the use of these probes for resistivity measurements and the methods employed to obtain related experimental data is given in the Appendix of this report.

Approximately one year after the research under the contract with the Environmental Protection Agency was completed, the second research program with the Tennessee Valley Authority was started. The objectives of this program were twofold: (1) to assist TVA in evaluating the planned installation of a sulfur trioxide injection facility in one power plant and (2) to investigate the use of ammonia conditioning in various other power plants. The research was to be concentrated on conditioning with ammonia for the purpose of elucidating the mechanisms of conditioning by this agent.

The interest of TVA in ammonia as a conditioning agent stems from the work of Reese and Greco,[5] who used ammonia successfully to improve the collection of fly ash produced from a high-sulfur coal. As pointed out in Section III of this report, Reese and Greco concluded that ammonia increased the resistivity of the fly ash from its normally low value either by neutralizing the surface layer of excess sulfur trioxide on the fly ash or by neutralizing sulfur trioxide in the gas phase and incidentally producing small solid or liquid particles of ammonium sulfate or ammonium bisulfate, as shown by the following equations:

$$2NH_3(g) + SO_3(g) + H_2O(g) \rightarrow (NH_4)_2SO_4(s)$$

$$NH_3(g) + SO_3(g) + H_2O(g) \rightarrow NH_4HSO_4(l,s)$$

The ammonium sulfate shown as the product of the first reaction would exist as a solid in a wide range of flue-gas temperatures, as indicated in the equation. The ammonium bisulfate shown as the product of the second reaction would exist as a liquid above 144°C or as a solid below this temperature; hence, the physical state is indicated in the equation as either liquid or solid. (There is some uncertainty about the temperature where ammonium bisulfate solidifies. The indicated temperature is based on the data of Kelley *et al.*[28] Thermodynamic information indicating that either of the two reactions can occur under flue-gas conditions is also included in the data published by Kelley.)

The initial investigation by Southern Research Institute failed to confirm either of the postulates. Another investigation by McLean[29] was also unsuccessful in determining the mechanism of ammonia conditioning under the circumstances encountered by Reese and Greco. Thus, additional research was undertaken at the Institute to elucidate the mechanism of ammonia conditioning.

ACCOMPLISHMENTS OF THE RESEARCH PROGRAMS

Under the program for EPA, conditioning by sulfur trioxide was investigated in ten precipitators in nine different power stations.[22] In several of these precipitators, only naturally occurring sulfur trioxide was available to condition the ash. However, in four precipitators, including three operated by the Public Service Company of Colorado, some method of injecting sulfur trioxide was available. For still another precipitator operated by another utility company during trials of sulfur trioxide as a conditioning agent for fly ash from a low-sulfur Western coal, the test data were acquired and compared with the data obtained by direct experimentation.

Under the program for TVA, a study was made of conditioning with sulfur trioxide in one of the TVA precipitators, and studies were also made of the conditioning with ammonia in four TVA precipitators in three different plants.[23]

A list of the more important power plants and their precipitators that were investigated during the two research programs is given in Table 1. Two plants can only be referred to by code numbers (Plants 3 and 6) because the utility companies permitted publication of the data from these two plants under the stipulation that neither the name nor location of either plant would be identified. The information in Table 1 includes properties of the coal burned at each plant, the flue-gas temperature in the precipitator, and very general descriptions of the properties of the fly ash.

Table 1. POWER PLANTS INVESTIGATED DURING THE RESEARCH ON THE CONDITIONING OF FLY ASH

	Plant					Coal			Fly ash	
No.[a]	Name	Unit	Precipitator[b]	Owner[c]	Conditioning agent	Wt % S	Wt % Ash	Gas temp, °C	log ρ[d]	pH[e]
1	Kingston	5	-	TVA	None[b]	2.1	19.6	175	12.0	6.1
2	Cherokee	2	-	PSCo	SO_3	0.6	7.9	143	11.2	7.0
3	(Not identified)	-	-	-	SO_3	~0.5	-	110	11.7	11.0
4	Cherokee	3	-	PSCo	SO_3	0.5	8.6	154	12.0	10.0
5	Arapahoe	4	-	PSCo	SO_3	0.5	5.9	135	12.6	11.1
6	(Not identified)	-	-	-	SO_3	0.6	11.8	160	12.3	8.1
7	Bull Run	1	1B	TVA	SO_3	0.8[g]	15.9[g]	125[g]	10.3[g]	4.8[g]
8	Widows Creek	7	7B	TVA	NH_3	0.9	17.6	132	11.5	5.2
9	Widows Creek	7	7A	TVA	NH_3	3.5	13.8	132	8.3	10.3
10	Bull Run	1	1C	TVA	NH_3	1.2	17.0	125	10.5	4.5
11	Gallatin	4	4C	TVA	NH_3	4.0	14.2	138	8.6	8.6

[a] Used for reference later in this report.

[b] Not listed if only one precipitator is used for the unit specified.

[c] TVA = Tennessee Valley Authority; PSCo = Public Service Company of Colorado.

[d] ρ = electrical resistivity, ohm cm (unconditioned ash).

[e] pH at equilibrium for a slurry consisting of 1 part of unconditioned ash and 300 parts of distilled water (weight proportions).

[f] Water vapor was investigated briefly as a conditioning agent.

SECTION V

RESULTS OF STUDIES OF CONDITIONING WITH SULFUR TRIOXIDE

The various studies of conditioning with sulfur trioxide can be logically classified by the source of the sulfur trioxide or the circumstances under which conditioning occurred (e.g., gas temperature and fly-ash composition). The first type of classification has been selected, more or less arbitrarily, as the basis for presenting the experimental results. Hence, the primary headings throughout this section designate the sources of sulfur trioxide, which are of four types: (1) the gas produced naturally by the combustion of a coal of moderate sulfur content and (2) the gases injected from (a) stabilized liquid sulfur trioxide, (b) concentrated liquid sulfuric acid, and (c) sulfur trioxide from the catalytic oxidation of sulfur dioxide.

CONDITIONING BY NATURALLY OCCURRING SULFUR TRIOXIDE

The Kingston plant in the TVA system was one of several plants investigated under Contract CPA 70-149 in which conditioning of fly ash occurred as the result of the presence of naturally occurring sulfur trioxide rather than the injection of this compound and, in limited experimentation, as the result of the injection of water vapor as a conditioning agent.[22] These data are of special interest because they show very well the interdependence of sulfur trioxide and water vapor in the normal process of conditioning and the importance of temperature in regard to the effectiveness of this process.

During the experimental work at the Kingston plant, the coal being burned in the unit under investigation, Unit 5, was of moderate sulfur content and moderate-to-high ash content. Analyses of various samples of the coal led to the following results as averages:

Sulfur, 2.1%
Ash, 19.6%

Determinations of the electrical resistivity of the fly ash entering the precipitator of Unit 5 were made with both a cyclone apparatus and the point-plane apparatus as the flue-gas temperature was varied through a wide range, roughly 150 to 190°C. The data were obtained with an electric field of 2.5 kV/cm in either resistivity device and are plotted in Figure 1. Several features of the data in this figure are of interest:

- Water vapor not injected. The resistivity values obtained with either apparatus reached a maximum at a temperature of about 175°C. The order of magnitude of the maximum was 1×10^{13} ohm cm with fly-ash samples in the cyclone apparatus and 1×10^{12} ohm cm with samples in the point-plane device. The appearance of maxima in both resistivity-temperature curves reflects the predominance of volume conduction at higher temperatures and surface conduction at lower temperatures.

- Water vapor injected. Resistivity values found at temperatures around 165°C were lowered substantially by the injection of water vapor. The reduction in resistivity was found to be one to two orders of magnitude, depending upon the method of measurement. To secure the resistivity data, water vapor was added by the crude method of pumping a stream of water into the boiler. It was intended that this process should essentially double the normal concentration of water vapor, about 7% by volume, that was produced from combustion of the coal, and it was found that this objective was satisfied as discussed in connection with flue-gas analyses in a following paragraph.

Samples of flue gas were collected at sampling ports ahead of the air preheater at a temperature of about 340°C and ahead of the precipitator at temperatures of about 150 to 190°C. The apparent concentrations of sulfur trioxide are plotted in Figure 2 and discussed in the next paragraph. The concentrations of sulfur dioxide averaged around 1500 ppm by volume, about as expected with a coal containing about 2% sulfur. The concentrations of water vapor averaged about 7% by volume without injection or 14% by volume with injection and thus showed the desired increase as the result of the injection process.

As indicated by Figure 2, the comparative values of sulfur trioxide ahead of the air preheater and ahead of the precipitator depended on the temperature at the latter location. At temperatures around 180°C, the concentration of sulfur

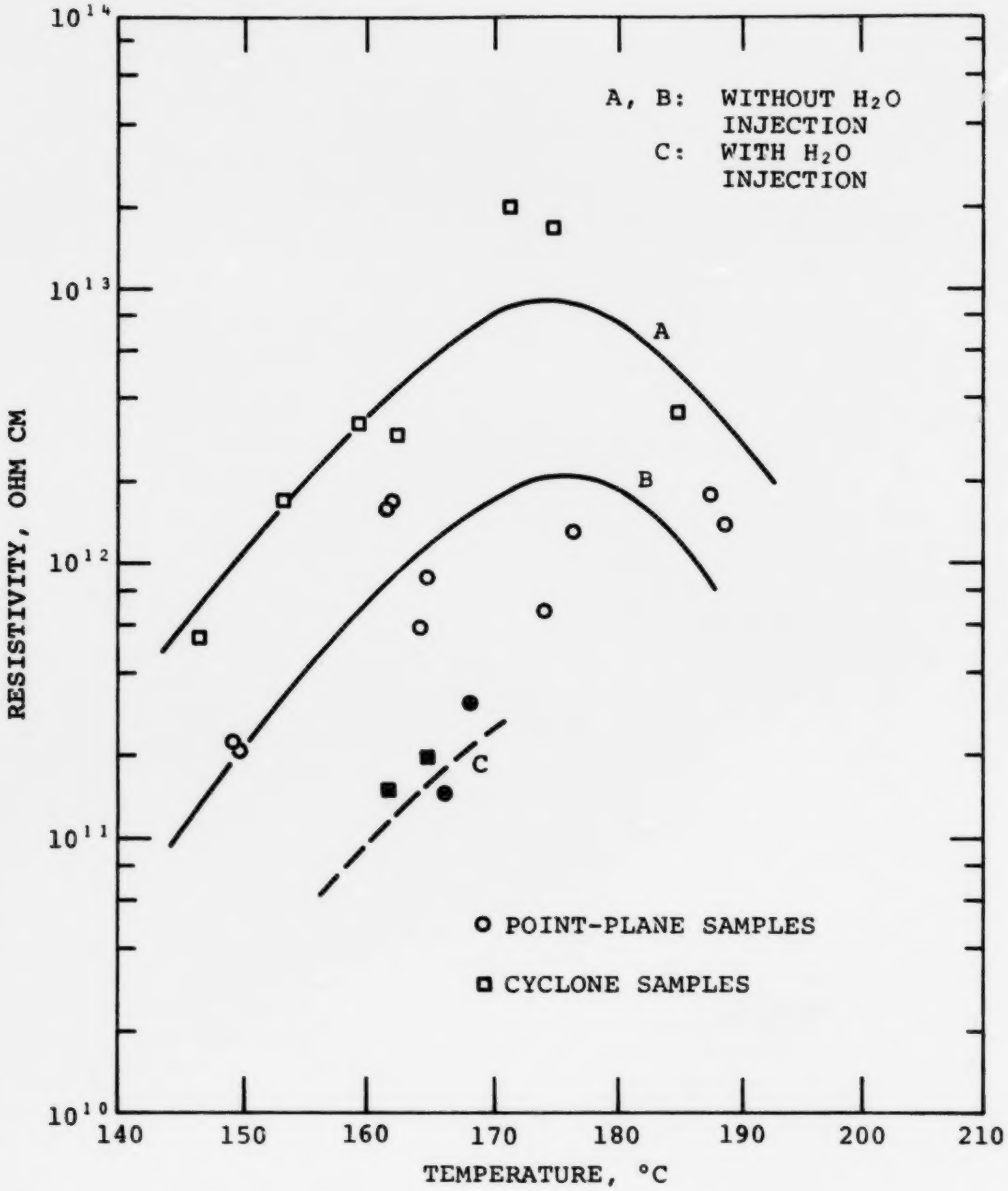

Figure 1. Electrical resistivity of fly ash at Kingston Unit 5

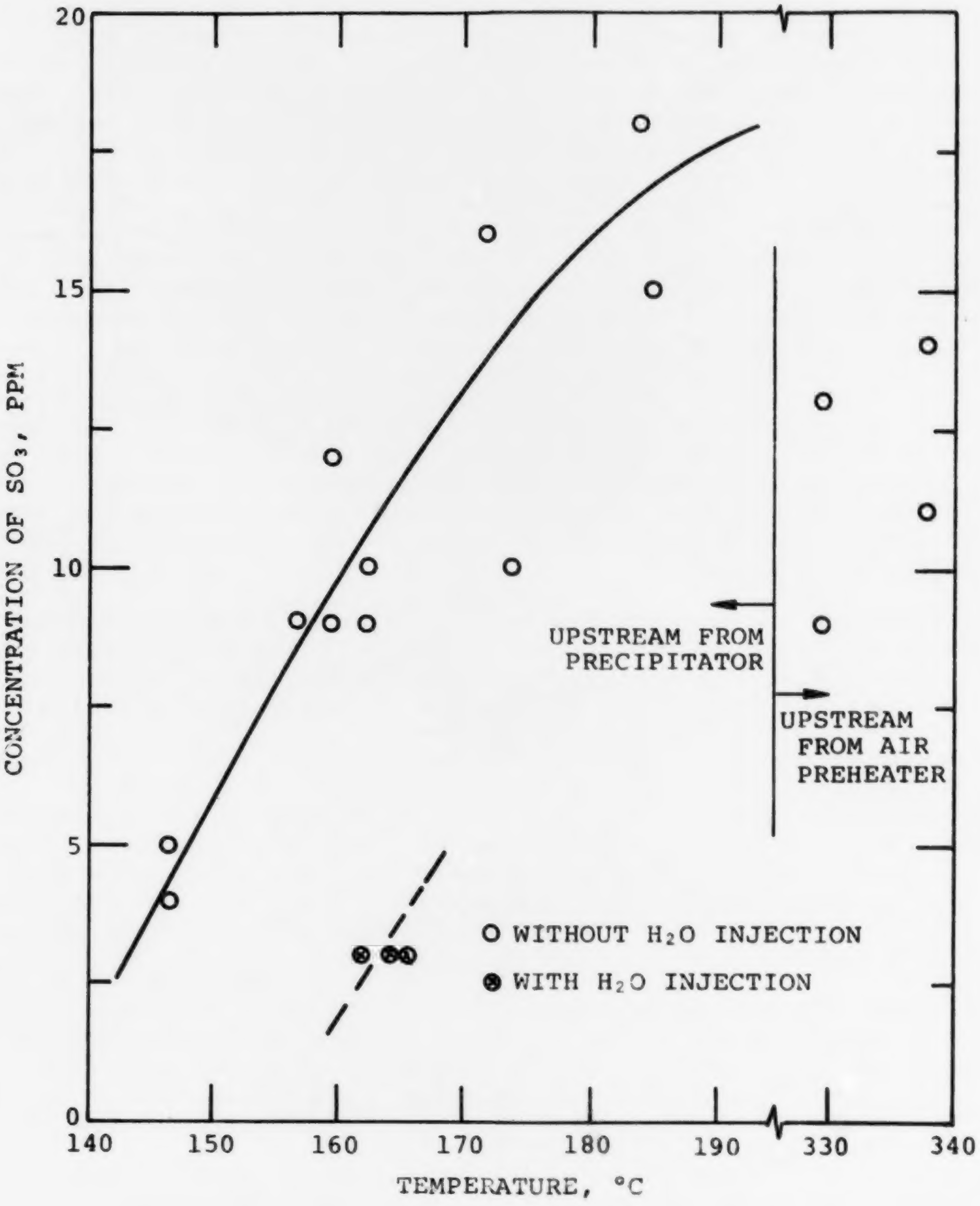

Figure 2. Concentrations of sulfur trioxide at Kingston Unit 5

trioxide at the inlet to the precipitator exceeded the concentration at the higher temperature upstream from the preheater. This difference was probably due to the reaction of sulfur dioxide and oxygen to produce sulfur trioxide within the preheater; this reaction is favored by the lowering of temperature and the availability of catalytically-active surfaces. As the temperature ahead of the precipitator became lower, however, the concentration of sulfur trioxide decreased. Moreover, when water vapor was injected, the concentration of sulfur trioxide decreased even more. Comparison of Figures 1 and 2 shows a marked correspondence between the values of fly-ash resistivity and sulfur trioxide concentration. It is apparent that decreases in resistivity values and sulfur trioxide concentrations occurred simultaneously. Decreases in both parameters were favored by decreasing temperature or increasing water-vapor concentration: they signify that increasing adsorption of sulfur trioxide and water vapor occurred on the surface of the fly-ash particles as either change occurred in the flue gas. The process of collection of sulfur trioxide by the ash was clearly adsorption rather than condensation, because the flue-gas temperature was consistently above the dew point of the sulfur trioxide-water mixture.[30,31]

Analyses of fly-ash samples collected in the two resistivity probes consisted of determinations of (1) the equilibrium pH of a slurry of 0.1 g of each sample with 30 ml of distilled water and (2) the weight percentage of the sample dissolved as sulfate ion. The results of the pH and sulfate determinations are shown in Figure 3. Although the data in this figure are scattered, they still give evidence of decreasing pH values and increasing sulfate concentrations as the collection temperature was lowered or as water vapor was injected. The indicated changes in pH and sulfate are consistent with the changes in the electrical resistivity of the ash and the concentration of sulfur trioxide in the flue gas as shown in Figures 1 and 2.

Analyses of fly ash from Kingston Unit 5 which show the overall composition are given in Table 2. The most noteworthy aspect of this composition—fairly typical of fly ash from Eastern coals—is the low percentage of calcium oxide compared with the percentages of lime in fly ash from Western coals, which are discussed later in this report.

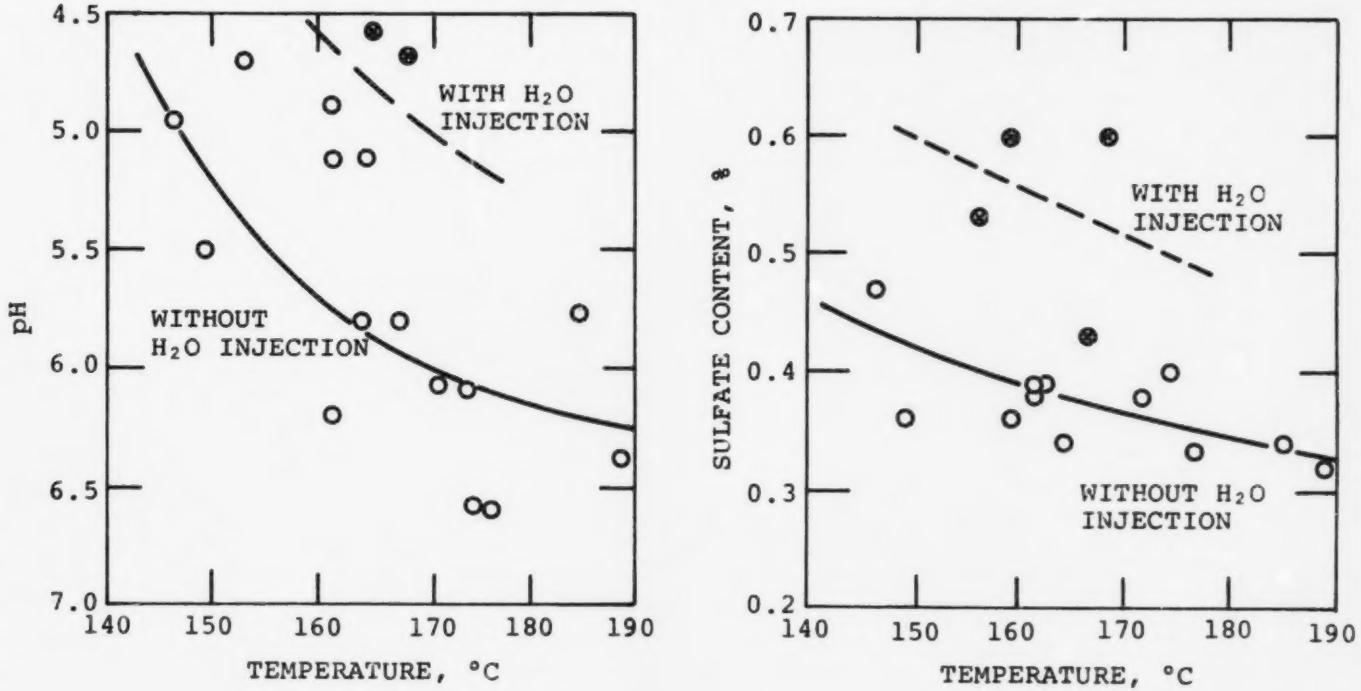

Figure 3. Chemical properties of fly ash at Kingston Unit 5

Table 2. COMPOSITION OF FLY ASH
FROM THE KINGSTON PLANT

Component	Weight percentage
Li_2O	0.06
Na_2O	0.42
K_2O	3.7
MgO	1.3
CaO	1.1
Al_2O_3	30.3
Fe_2O_3	9.9
SiO_2	52.4
TiO_2	1.7
P_2O_5	0.51
SO_3	0.45

CONDITIONING BY THE INJECTION OF VAPOR FROM STABILIZED LIQUID SULFUR TRIOXIDE

The most frequently used source of sulfur trioxide for conditioning fly ash, particularly in foreign power plants, has been the stabilized liquid form of this compound. The stabilized compound is available in the United States as the product of Allied Chemical Corporation known as "Sulfan." Despite the fact that injection systems based on liquid sulfur trioxide have been widely used, only one system of this type was available for investigation under Contract CPA 70-149.[22] This system was in use at Unit 2 of the Cherokee plant of the Public Service Company of Colorado. However, limited data from another plant with a Sulfan system (referred to as Plant 3) were made available by another Western utility company and are included in a later section of this report.

Cherokee Plant, Unit 2

The Cherokee plant of the Public Service Company of Colorado consists of four units with power-production ratings varying from 100 to 350 MW. During 1971, the installation of a Sulfan injection system to treat flue gas from three units—Units 1, 2, and 4—was completed. During July of 1971, shortly after service to Unit 2 was started, the investigation described in this report was carried out at that unit. Unit 2 is rated at 110 MW, and it is equipped with both a mechanical collector and an electrostatic precipitator. Sulfur trioxide is injected into the duct between these two gas-cleaning devices.

The coal burned at the Cherokee station is normally a low-sulfur coal from Routt County, Colorado. It produces a high-resistivity fly ash that requires conditioning for effective collection in an electrostatic precipitator. Measured values of resistivity of the unconditioned ash have ranged from 1.6×10^{11} ohm cm at 143°C in Unit 2 to 1.0×10^{12} ohm cm at 154°C in Unit 3 of the Cherokee station.

At the time the conditioning study was carried out at Cherokee Unit 2, a sample of the coal was analyzed and found to have the following properties:

Sulfur, 0.6%
Ash, 7.9%

These values appear to be fairly representative, for they agree with values obtained on another occasion when a study was made of conditioning at Cherokee Unit 3.

The point-plane probe was used for all of the resistivity determinations at Cherokee Unit 2. Considerable difficulty was encountered in making these determinations because of the presence of an abnormally high concentration of unburned carbon in the ash and the tendency of the fly-ash samples to undergo electrical breakdown even at very low applied fields. The only available means of overcoming this difficulty was to make measurements at very low electric fields, of the order of 0.1 kV/cm or less. (In other plants, resistivity data were usually taken at substantially higher fields, which have the effect of lowering the apparent values of resistivity as discussed by Nichols.[27])

The resistivity data obtained without the injection of sulfur trioxide and with the injection of this agent at concentrations of 13 and 27 ppm* are presented in Table 3. Later in this report (Figure 18, page 120), the data are shown graphically in comparison with data from other plants. Both the table and the figure indicate that 13 ppm of sulfur trioxide depressed the resistivity to a greater degree than was necessary and suggest that a concentration of only 5 ppm might have been adequate. Unfortunately, determinations of the

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*These concentrations were reported by the plant operators, as were the concentrations of conditioning agents in most of the other plants investigated. The only experimental determinations of concentrations of conditioning agents that were made by personnel of Southern Research Institute are discussed explicity later in this report.

Table 3. ELECTRICAL RESISTIVITY OF FLY ASH AT CHEROKEE UNI

Injected SO_3 concn, ppm	Resistivity,[a] ohm cm
0	1.6×10^{11}
13	1.4×10^{7}
13	5.6×10^{7}
27	2.5×10^{7}
27	3.8×10^{7}
27	5.0×10^{7}

[a] Temperature, 143°C.

resistivity at concentrations below 13 ppm could not be made because a failure in the injection system caused an extended interruption in its use.

The effect of sulfur trioxide on the resistivity of the ash had the expected corollary effect on the precipitator voltages, currents, and spark rates. For the inlet section of the precipitator, the time-average voltage and current were 37 kV and 80 mA at a spark rate of 25/min without injection of sulfur trioxide. For the same section, the values were 41 kV and 720 mA at a spark rate of only 5/min with injection of 27 ppm of the conditioning agent.

Concentrations of flue gases with and without injection are given in Table 4. These data show that the concentrations of sulfur trioxide ahead of the air preheater and ahead of the precipitator were quite low without injection, only 2 to 3 ppm. The concentration at the entrance of the precipitator (downstream from the plane of injection), however, increased sharply with injection. Indeed, the concentration reached values almost as high as the reported injection values, suggesting that only a small fraction of the conditioning agent was collected on the surface of the fly-ash particles, at least at the precipitator inlet. Thus, the flue-gas analyses as well as the resistivity data give evidence of excessive rates of injection of sulfur trioxide.

Information about the properties of the fly ash is given in Table 5. The pH and sulfate values indicate that a substantial pickup of the normally occurring sulfur trioxide by the fly ash occurred during passage of the ash through the air preheater. The decrease in pH and the increase in sulfate

Table 4. CONCENTRATIONS OF FLUE GASES AT CHEROKEE UNIT 2

Injected SO_3 concn, ppm	Temp,[a] °C	Concentrations		
		SO_3, ppm	SO_2, ppm	H_2O, %
0	368	2	507	-
	368	2	512	-
	143	3	473	-
13	143	12	452	7.4
	143	11	442	-
27	143	26	460	7.5
	143	23	420	-

[a] The higher temperature indicates sample collection upstream from the air preheater. The lower temperature is for the flue gas entering the precipitator.

Table 5. CHEMICAL PROPERTIES OF FLY ASH AT CHEROKEE UNIT 2

Injected SO_3 concn, ppm	Temp,[a] °C	Ash properties	
		pH	Sulfate, wt %
0	368	10.1[b]	0.29[b]
	143	7.3	0.97
	143	6.6	1.28
13	143	6.8	1.42
	143	6.9	1.51
	143	6.9[b]	1.53[b]
27	143	7.1	1.85
	143	6.7	1.76
	143	7.4	1.89

[a] The higher temperature indicates sample collection upstream from the air preheater. The lower temperature is for the flue gas entering the precipitator.

[b] The samples having these properties were collected in a cyclone sampler; all other samples were collected with the point-plane resistivity probe.

concentration may have been influenced to some degree, however, by the removal in the mechanical collector of coarse fly-ash particles with a lower-than-average surface-to-mass ratio. The pH and sulfate data obtained for conditioned ash show no significant change in pH but show the significant increase in sulfate concentration that was expected. It is to be noted that pH data for slurries of fly ash in water are not necessarily valid indicators of the surface properties of the ash. Frequently, the pH values of slurries are lower when contact is first made between ash and water than when equilibrium is reached after prolonged stirring. The explanation for this phenomenon is assumed to be the existence of an acid film on the surface and the presence of soluble excess base in the interior of the ash particles. It is to be noted further that although sharp increases in sulfate concentrations were produced by the injection of sulfur trioxide, they corresponded to small fractions of the concentrations injected. A reasonable estimate of the fly-ash concentration treated is 2.3 g/m^3 (1 gr/ft^3); the increased sulfate for this amount of fly ash would require concentrations of only 1 to 2 ppm of sulfur trioxide in the flue gas.

As a result of the unexpected brevity of the investigation at Cherokee Unit 2, no sample of fly ash large enough for complete analysis was collected. Hence, the only data for the overall composition that can be cited was obtained on another occasion in an investigation of Unit 3. These data are given in Table 6. There is at least a possibility that the composition shown in Table 6 is not representative of the ash that was conditioned at Unit 2. The basis for emphasizing this possibility is that the ash from Unit 3 was substantially more basic than the ash from Unit 2. A possible explanation for this difference other than an actual difference in composition is that the ash was collected at a somewhat higher temperature at Unit 3 (154°C rather than 143°C) and may thus have gained less acid by the adsorption of normally occurring sulfur trioxide.

It is of interest to cite the results of conditioning at Cherokee Unit 2 as recently reported by the representatives of the utility company.[25] The reported efficiencies of the precipitator operating at full load (110 MW) are 94.0% without conditioning and 95.2% with conditioning at a concentration of about 15 to 20 ppm. These efficiencies are to be compared with a design value of 94.2% at a gas velocity of 1.51 m/sec (4.95 ft/sec) and a specific collecting area of 31.3 m^2/(m^3/sec) (159 ft^2/[1000 ft^2/min]). The effect of conditioning in the instance of Cherokee Unit 2 is thus not very dramatic. (It is to be noted that the efficiencies cited are for the precipitator alone, not the combination of mechanical collector and precipitator.)

Table 6. COMPOSITION OF FLY ASH
FROM THE CHEROKEE PLANT[a]

Component	Weight percentage
Li_2O	0.02
Na_2O	1.7
K_2O	1.2
MgO	1.9
CaO	6.8
Al_2O_3	25.7
Fe_2O_3	4.8
SiO_2	54.6
TiO_2	1.1
P_2O_5	1.0
SO_3	1.0

[a] Collected at Unit 3 of the Cherokee plant and assumed to be representative of fly ash from Unit 2, although no information for fly ash obtained directly from Unit 2 is available.

Plant 3

The data for this plant were provided for this study with the understanding that the name of the plant and the operating utility company would not be cited in the Institute's reports. All of the data subsequently presented, except that dealing with the fly-ash composition, were obtained by the utility company.

Plant 3 is located in one of the Western states and burns a low-sulfur coal that is typical of that region. It does not employ a mechanical collector; it uses only an electrostatic precipitator for gas cleaning, and the precipitator operates at 110°C. Despite the low temperature, the resistivity of the fly ash is high enough to warrant conditioning of the ash. Trials were thus made with sulfur trioxide as the conditioning agent and with Sulfan as the source of the agent.

The results of some of the trials of sulfur trioxide conditioning are shown in Table 7. Clearly, the addition of the conditioning agent lowered the resistivity of the ash and increased the sulfate content. No information relative to the flue-gas composition, however, is available for presentation.

Table 7. ELECTRICAL RESISTIVITY AND SULFATE CONTENT OF FLY ASH AT PLANT 3

Injected SO_3 concn, ppm	Resistivity,[a] ohm cm	Sulfate, wt %
0	4.5×10^{11}	0.17
10	2.3×10^{10}	0.31
18-20	7.0×10^{9}	0.38

[a] Determined with a point-plane apparatus at an unspecified electric field with the temperature near 110°C.

A sample of fly ash from Plant 3 was obtained and analyzed at Southern Research Institute. It is not known whether this ash had the same composition as the ash that was conditioned, but the results of the analysis showing the weight percentages of the major constituents are presented in Table 8. The ash that was analyzed was highly basic; it produced a pH value of about 11 in a slurry with distilled water.

Table 8. COMPOSITION OF FLY ASH FROM PLANT 3

Component[a]	Weight percentage
CaO	6.3
Al_2O_3	29.6
Fe_2O_3	3.8
SiO_2	53.0

[a] Only a limited number of the components were determined, as in the analyses of some of the other samples of ash discussed later in this report.

CONDITIONING BY THE INJECTION OF VAPOR FROM CONCENTRATED SULFURIC ACID

Sulfuric acid is an alternative to stabilized liquid sulfur trioxide as a source of sulfur trioxide for conditioning fly ash. The acid is a more commonly used chemical commodity than stabilized liquid sulfur trioxide. It is customarily available for industrial use as a mixture of sulfuric acid with water, typically 93 wt-% acid and 7 wt-% water (known as 66°Bé acid).

One of the disadvantages of sulfuric acid is that this compound requires higher temperatures for vaporization than sulfur trioxide. The boiling points of mixtures of the acid with water vary with the proportions of the components that are present. The maximum boiling point is approximately 325°C for an azeotropic mixture consisting of about 98.5% of the acid and 1.5% of water.[31] Of course, in a vaporizer swept with a carrier gas such as dry air, vaporization will produce partial pressures of sulfuric acid and water totaling less than 1 atm at temperatures below the normal boiling point of the mixture being used.

Sometimes the vaporization of sulfuric acid is accompanied by the decomposition of the vapor of the acid to the vapors of sulfur trioxide and water, as shown by the following equation:

$$H_2SO_4(g) \longrightarrow SO_3(g) + H_2O(g)$$

The extent of decomposition depends upon the partial pressure of sulfuric acid produced and the concentration of water vapor present in the vaporizer, as well as the temperature of the carrier gas used to sweep the vaporizer. The extent of decomposition of the vapor produced from the azeotrope at the normal boiling point (about 325°C, the temperature of vaporization in the absence of carrier gas) is about 40%.[31] The extent of decomposition decreases as the temperature is lowered or as the partial pressure of sulfuric acid or water vapor is increased. The extent of decomposition under any specified conditions can be calculated from the thermodynamic data in the JANAF Tables.[7] In the vaporization of sulfuric acid, extremely high temperatures must be avoided to prevent the decomposition of the acid vapor to sulfur dioxide, oxygen, and water vapor, as shown by this equation:

$$H_2SO_4(g) \longrightarrow SO_2(g) + \frac{1}{2}O_2(g) + H_2O(g)$$

If dry air is the carrier gas sweeping the vaporizer, the decomposition as shown above becomes extensive at temperatures above 650°C.[32]

Cherokee Plant, Unit 3

Whereas Units 1, 2, and 4 of the Cherokee plant were equipped with a Sulfan injection system during 1971, as stated previously on page 26, Unit 3 of this plant was equipped with a sulfuric-acid injection system the previous year. A study of conditioning at Cherokee Unit 3, a 150-MW plant, was conducted during October of 1970 when the injection manifold was located in the duct upstream from the mechanical collector. Later during the year, the injection manifold was temporarily relocated in the duct between the mechanical collector and the electrostatic precipitator in an effort to improve the effectiveness of the conditioning system. No measurements of the electrical resistivity were made while the injection manifold was relocated; however, analyses were made of fly-ash samples taken from the hoppers of the ash collection system at that time.

In the injection system at Cherokee Unit 3, the sulfuric acid was commercial 66°Bé acid. The acid was vaporized with hot combustion gases from a natural-gas burner; the inlet and outlet temperatures of the gas stream passing through the vaporizer were about 540 and 370°C, respectively. The gas stream passing from the vaporizer to the injection nozzles was heated to avoid condensation of the acid vapor. The estimated ratio of the partial pressure of sulfur trioxide to the partial pressure of sulfuric acid was 12.4:1.0, based on the assumption that the gas stream leaving the vaporizer had a temperature of 370°C and a water-vapor partial pressure of 0.05 atm (produced mostly by the combustion of natural gas and increased only slightly by the partial decomposition of the acid vapor).

Analyses of the coal being burned at Cherokee Unit 3 during the conditioning studies yielded these results:

Sulfur, 0.5%
Ash, 8.6%

These concentrations of sulfur and ash are close to the values for coal from the same source—Routt County, Colorado—that was sampled at Unit 2 on another occasion (page 27).

Two series of resistivity determinations were made, one with only coal as the fuel and another with a mixture of coal and natural gas as fuels. In both series, resistivity devices of the cyclone type were employed, and resistivity values were determined at an applied electric field of about 2.5 kV/cm. The results of the determinations are given in Table 9. They indicate that very little change in resistivity occurred, despite the fact that the concentrations of injected sulfuric acid ranged up to 33 ppm on one occasion and 44 ppm on another occasion.

The results of flue-gas analyses are given in Table 10. The data for sulfur dioxide show the expected increase in concentration as the fuel was changed from coal and natural gas to

Table 9. ELECTRICAL RESISTIVITY OF FLY ASH AT CHEROKEE UNIT 3
(Validity questionable as discussed in text)

Temp,[a] °C	Injected H_2SO_4 concn, ppm	Resistivity, ohm cm
149	0	2.0×10^{12}
	6	9.3×10^{11}
	17	7.8×10^{11}
	26	5.6×10^{11}
	33	5.0×10^{11}
154	0	1.0×10^{12}
	13	1.0×10^{12}
	26	6.0×10^{11}
	33	6.3×10^{11}
	44	6.6×10^{11}

[a] The lower temperature was recorded with a mixture of coal and natural gas as the fuel. The higher temperature was recorded with only coal as the fuel.

coal alone. The data for sulfur trioxide indicate that little of this substance was present under any of the sampling conditions, not even when the maximum concentrations of sulfuric acid were injected.

The results of determinations of pH and dissolved sulfate in aqueous slurries of the samples of fly ash that had been collected for resistivity determinations are given in Table 11. These data indicate that slight decreases in pH and increases in sulfate concentration occurred as the result of the injection of sulfuric acid. The increases in sulfate are quite small in comparison with the increases that would have been found if all of the injected sulfuric acid had been deposited on the ash. If it is assumed that the concentration of fly ash treated with sulfuric acid ahead of the mechanical collector was about 0.9 g/m^3 (0.4 gr/ft^3), the deposition of 44 ppm of sulfuric acid on the ash would have increased the sulfate concentration by about 12%, whereas the reported injection of 44 ppm of sulfuric acid caused an actual increase of only 0.35%.

In view of the fact that the sulfuric acid injected could not be accounted for by analysis of either flue gas or fly ash in the duct entering the electrostatic precipitator, analyses were made of fly ash from the hoppers of the mechanical

Table 10. CONCENTRATIONS OF FLUE GASES AT CHEROKEE UNIT 3

Temp,[a] °C	Injected H_2SO_4 concn, ppm	Concentrations		
		SO_3, ppm	SO_2, ppm	H_2O, %
395	0	2	226	-
149	0	<1	222	9.5
	6	<1	222	-
	17	<1	210	-
	26	<1	217	-
	33	2	216	-
395	0	<1	314	-
154	0	1	358	-
	13	1	357	7.7
	26	<1	349	-
	33	2	349	-
	44	3	357	8.4

[a] The temperature of 395°C indicates sampling upstream from the air preheater, and the temperatures of 149 and 154°C indicate sampling at the precipitator inlet. The temperature at the latter location was 149°C with coal and natural gas as a mixed fuel or 154°C with coal only as the fuel.

Table 11. CHEMICAL PROPERTIES OF FLY ASH AT CHEROKEE UNIT 3

Injected H_2SO_4 concn, ppm	Ash properties[a]	
	pH	Sulfate, wt %
0	10.0	0.77
13	9.9	0.90
26	9.9	1.09
33	9.8	1.00
44	9.5	1.12

[a] For samples collected at the precipitator inlet at a temperature of 154°C.

collector and the electrostatic precipitator. The first samples were collected with the injection manifold in its original location upstream from the mechanical collector. In these samples, the material from the mechanical collector was expected to have a disproportionately high concentration of sulfate, accounting for the absence of the injected sulfuric acid in the duct entering the precipitator; however, the analysis of this material failed to show the expected contrast with the analysis of the material from the precipitator. Later hopper samples were collected after the injection manifold had been moved temporarily to the duct between the mechanical collector and the precipitator. As expected, analysis of these samples showed that the injection of sulfuric acid did not alter the sulfate content of the ash collected mechanically; surprisingly, however, these analyses showed that the injection of sulfuric acid also did not change the sulfate content of the ash collected by electrostatic precipitation.

It seems obvious that there was a fundamental difficulty at Cherokee Unit 3 in injecting sulfuric acid in an effective form at the intended concentrations. A possible cause of the difficulty was improper temperature control in the vaporizer or the manifold leading to the injection nozzles. Excessive temperatures could have caused sulfur trioxide to decompose to sulfur dioxide; however, temperatures in excess of 650°C would have been required for this decomposition process to occur, and temperatures in this range were not observed. Low temperatures in the injection manifold could have allowed the sulfuric acid vapor to condense with water vapor to a liquid; if this process had occurred, the manifold would have been flooded, and no such problem was reported. Another possible cause of ineffective conditioning would be poor dispersal of the injected gas stream within the flue gas, permitting condensation of sulfuric acid and water vapor to occur within the duct at the relatively low temperature and the increased partial pressure of water in the flue gas. Condensation of acid within the duct is a plausible explanation for inefficient conditioning of the fly ash; however, no evidence of condensation was reported.

Despite the evident difficulties in injecting sulfuric acid in an effective form, representatives of the Public Service Company have reported that the injection of sulfuric acid at a calculated rate of 15 to 20 ppm has increased the precipitator efficiency from 37.5 to 51.4%.[25] These efficiency values are for the precipitator alone; they do not take into account the fly ash removed upstream by the mechanical collector.

Arapahoe Plant, Unit 4

Unit 4 of the Arapahoe plant (100 MW) was the first of the four units of that plant to have gas-conditioning facilities. A study of conditioning at Unit 4 was conducted in October of 1970, immediately after the previously described work at Cherokee Unit 3 was completed. At the time of the study at Arapahoe Unit 4, the vapor from 66°Bé sulfuric acid was injected into the duct between the mechanical collector and the electrostatic precipitator.

The vaporizer for sulfuric acid at Arapahoe Unit 4 differed from that at Cherokee Unit 3 in that a stream of ambient air was electrically heated to 255°C and used to sweep the vaporizer and enter the injection manifold at 230°C. Thus, the vaporizer at the Arapahoe plant had a lower temperature and a lower background partial pressure of water (less than 0.03 atm and probably as low as 0.01 atm), and it produced a much lower vapor ratio of sulfur trioxide to sulfuric acid, only about 0.3:1.0. These vapors were injected into the flue gas at a temperature of 135°C.

Low-sulfur coals from Weld County, Colorado, and Hanna County, Wyoming, are normally burned at Arapahoe Unit 4. The sulfur and ash percentages are represented by the following data for coal samples collected in October of 1970:

Sulfur,	0.5%
Ash,	5.9%

The composition of fly ash produced from this coal is shown in Table 12. Although the results of the coal analysis are similar to the data for coal used at the Cherokee plant (pages 27 and 34), the results of the ash analysis are substantially different, particularly with respect to the base calcium oxide (page 31). The concentration of calcium oxide in the ash was far higher at the Arapahoe plant than at the Cherokee plant.

The results of determinations of the electrical resistivities of unconditioned and conditioned ash at Arapahoe Unit 4 are given in Table 13. These data were obtained with a cyclone probe and an electric field of about 2.5 kV/cm across the ash samples. The data show clearly that the resistivity of the ash was quite high without conditioning but was reduced significantly with conditioning by sulfuric acid.

The results of flue-gas analyses are shown in Table 14. The data for sulfur trioxide, which are the results of greatest interest, showed that only minor increases occurred as sulfuric acid was injected into the gas stream.

Table 12. COMPOSITION OF FLY ASH FROM ARAPAHOE UNIT 4

Component	Weight percentage
K_2O	0.8
MgO	4.2
CaO	15.6
Al_2O_3	19.0
Fe_2O_3	7.3
SiO_2	36.1

Table 13. ELECTRICAL RESISTIVITY OF FLY ASH AT ARAPAHOE UNIT 4

Injected H_2SO_4 concn, ppm	Resistivity,[a] ohm cm
0	3.8×10^{12}
6	5.7×10^{10}
12	3.2×10^{10}
18	1.9×10^{10}

[a] Temperature, 135°C.

Table 14. CONCENTRATIONS OF FLUE GASES AT ARAPAHOE UNIT 4

Injected H_2SO_4 concn, ppm	Concentrations[a]		
	SO_3, ppm	SO_2, ppm	H_2O, %
0	<1	387	8.9
6	1	446	-
12	2	413	8.8
18	2	430	-

[a] For samples collected at the precipitator inlet at a temperature of 135°C.

Information about the effect of injected sulfuric acid on the chemical properties of the fly ash is given in Table 15. The pH data in this table show that slight reductions in the basicity of the ash occurred with acid injection. The sulfate contents of the ash show a much more pronounced change with acid injection, increasing from 1.00% without injection to 2.97% at the highest level of injection. The increases in the sulfate content of the ash can be compared with the theoretical values based on an assumed ash concentration of 1.2 g/m^3 (0.5 gr/ft^3) between the mechanical collector and the electrostatic precipitator (the location of the injection manifold) and a virtually complete pickup of the injected acid by the ash (little acid remained in the gas phase, as shown by Table 14). The theoretical increase in sulfate content at an injected acid concentration of 18 ppm is 4.3%, whereas the observed increase was 1.5%. Although the ratio of these values is 3:1, the efficiency of sulfuric-acid conditioning at Arapahoe Unit 4 appears to have been much greater than that of Cherokee Unit 3 on the bases of both chemical analyses and resistivity determinations. However, the efficiency data reported by the Public Service Company show a less striking difference. For Arapahoe Unit 4, the reported increase in efficiency was from 67.3 to 77.3%; for Cherokee Unit 3, the increase was from 37.5 to 51.4%.[25]

Table 15. CHEMICAL PROPERTIES OF FLY ASH AT ARAPAHOE UNIT 4

Injected H_2SO_4 concn, ppm	Ash properties[a]	
	pH	Sulfate, wt %
0	11.1	1.50
6	11.1	2.23
12	10.0	2.50
18	10.8	2.97

[a] For samples collected at the precipitator inlet at a temperature of 135°C.

Plant 6

The power station referred to as Plant 6 has several units. One of these units with a rating of 140 MW was being operated experimentally with a sulfuric acid injection system during the early part of 1971. The acid injection system functioned in essentially the same manner as the one at Arapahoe Unit 4. The sulfuric acid vaporized was 66°Bé commercial acid, and the vaporizer operated with electrically heated air entering at 260°C and leaving at 205°C. The vapor ratio of sulfur trioxide to sulfuric acid was slightly lower than that at Arapahoe Unit 4 as the result of the lower temperature of the gas stream leaving the vaporizer.

The circumstances for conditioning at Plant 6 differed from those at Arapahoe Unit 4 in several respects. First, Plant 6 had no mechanical collector and thus essentially all of the fly ash produced in the boiler was subjected to conditioning. Second, Plant 6 had a higher gas temperature, 160°C rather than 135°C. Finally, Plant 6 produced a much less basic fly ash than Arapahoe Unit 4

Analyses of coal samples collected during the investigation at Plant 6 led to the following results:

Sulfur, 0.6%
Ash, 11.8%

Analysis of the fly ash produced at Plant 6 gave the results listed in Table 16. The analytical data show that the sulfur percentage in the coal burned at Plant 6 (from West Virginia) was similar to the coals burned at the plants in the West but that the fly ash produced from the Eastern coal was distinctly different from the ash produced from the Western coals, principally in having a much lower weight percentage of the basic constituent calcium oxide.

Table 16. COMPOSITION OF FLY ASH FROM PLANT 6

Component	Weight percentage
Li_2O	0.09
Na_2O	0.51
K_2O	3.8
MgO	1.3
CaO	0.68
Al_2O_3	30.2
Fe_2O_3	4.9
SiO_2	53.0
TiO_2	2.0
P_2O_5	0.17
SO_3	0.36

The results of determinations of the electrical resistivity of the fly ash and analytical work with the flue gas and the fly ash are presented in Tables 17, 18, and 19. The principal points of interest shown by the data in these tables are as follows:

- Injection of sulfuric acid at increasingly higher concentrations gradually lowered the resistivity of the ash from 2×10^{12} ohm cm to a value around 1×10^{10} ohm cm.
- Most of the injected acid remained in the gas stream, as indicated by the determinations of sulfur trioxide.
- Injection of the acid lowered the pH produced by the fly ash in an aqueous slurry from a weakly basic value to values in the acid range. However, it caused a very small increase in the sulfate content of the ash.

CONDITIONING BY THE INJECTION OF SULFUR TRIOXIDE PRODUCED BY THE CATALYTIC OXIDATION OF SULFUR DIOXIDE

The catalytic oxidation of sulfur dioxide to the trioxide is being used with increasing frequence as a method of obtaining the trioxide for fly-ash conditioning. The process can be effected by the use of a catalyst of vanadium pentoxide operating between temperature limits of about 425 and 550°C. A high temperature is desirable to enhance the effect of the catalyst on the rate of oxidation of the sulfur dioxide. However, there is a maximum in the temperature that can be used, for the oxidation process becomes gradually subject to thermodynamic hindrance as temperature is increased.[32]

Studies were carried out with conditioning systems of the type described above on two occasions at the Bull Run plant of the Tennessee Valley Authority. Initially, the system in use at this 900 MW plant treated only 25% of the effluent fly ash as it passed through one of the four electrostatic precipitators. Later, the initial system was replaced with a larger system capable of treating the fly ash entering all four precipitators. All of the studies described in this report, however, were conducted at the same precipitator, referred to as Collector 1B.

Apparent Need for Conditioning at the Bull Run Plant

Research conducted by TVA personnel over a period of several years showed that a decrease in precipitation efficiency occurred as the sulfur content of the coal was lowered. In acceptance tests of Collector 1B in 1969 with 2.25%-sulfur

Table 17. ELECTRICAL RESISTIVITY OF FLY ASH AT PLANT 6

Injected H_2SO_4 concn, ppm	Type of resistivity probe[a]	Resistivity, ohm cm
0	C	2.0×10^{12}
	C	2.0×10^{12}
4	C	1.2×10^{11}
	P	0.7×10^{11}
	C	1.8×10^{11}
	P	2.0×10^{11}
	C	1.5×10^{11}
8	P	1.4×10^{11}
	C	1.3×10^{11}
	P	2.1×10^{11}
	C	1.6×10^{11}
16	P	1.1×10^{10}
	C	0.1×10^{10}
	P	2.5×10^{10}
	C	0.2×10^{10}

[a] C and P indicate cyclone and point-plant sampling probes, respectively, which were used at the precipitator inlet at a temperature of 160°C. Electric fields used for the resistivity determinations averaged about 3 kV/cm.

Table 18. CONCENTRATIONS OF FLUE GASES AT PLANT 6

Injected H_2SO_4 concn, ppm	Concentrations[a]		
	SO_3, ppm	SO_2, ppm	H_2O, %
0	<1	373	7.7
	<1	384	-
4	-	397	7.3
	4	391	-
8	6	391	7.7
	11	475	-
16	14	488	7.9
	12	470	-

[a] For samples collected at the precipitator inlet at a temperature of 160°C.

Table 19. CHEMICAL PROPERTIES OF FLY ASH AT PLANT 6

Injected H_2SO_4 concn, ppm	Ash properties[a]	
	pH	Sulfate, wt %
0	8.1	0.24
4	6.1	0.32
8	5.1	0.38
16	4.4	0.43

[a] For samples collected at the precipitator inlet at a temperature of 160°C.

coal as the fuel, the results showed that the manufacturer's guarantee of 99% efficiency was satisfied under full-load conditions. In performance tests in 1971 with relatively low-sulfur coals, substantial decreases in efficiency were observed.[33] With so-called "Bull Run" coal containing 1.2 to 1.6% sulfur, the efficiency of Collector 1B was determined under reduced-load conditions, and it was estimated as only 90% at full load. With "Haddix" coal from Eastern Kentucky, containing only 0.9% sulfur, the efficiency predicted at full load was reduced further to only 80%.

These marked losses in efficiency led to the trial of conditioning first with sulfur trioxide and then with ammonia in Collectors 1B and 1C, respectively. The greater success achieved with sulfur trioxide led to an enlargement in the conditioning facilities for this agent to permit treatment of fly ash entering all four collectors.

All of the collection of fly ash at the Bull Run plant is accomplished with electrostatic precipitators. Thus, sulfur trioxide is injected into the flue gas ahead of each precipitator at a location between the air preheater and the precipitator. At this location, the mean flue gas temperature is normally about 125°C.

Results of the First Investigation (1972)

The first investigation of conditioning at the Bull Run plant was conducted during August of 1972 immediately after the original facilities for injecting sulfur trioxide were placed in operation. During this investigation, experimental work including tasks other than determinations of fly-ash resistivity and analyses of coal, fly ash, and flue gas were undertaken for the first time with the assistance of TVA personnel. These additional tasks included determinations of precipitator efficiency with and without conditioning by direct determinations of inlet and outlet fly-ash concentrations and indirect determinations with light-obscuration devices at the outlet. They also included systematic determinations of electrical parameters of the precipitator with and without conditioning.

Coal and Fly-Ash Compositions—

TVA's intention was that low-sulfur coal would be burned at the Bull Run plant during the joint experimental efforts by TVA and Institute personnel. However, the shortage of this coal made it necessary to burn "reclaim" coal—that is, reserve coal consisting of a mixture from various sources. Thus, the composition of the coal varied more widely than desired. The sulfur content varied from 0.9 to 1.6%, and the ash content varied from 14.5 to 15.3%. The average concentrations were as follows:

Sulfur, 1.2%
Ash, 15.3%

Analyses of fly-ash samples collected at the precipitator inlet in alundum thimbles yielded more consistent results than analyses of the coal. A representative composition is given in Table 20. The most striking aspect of this

Table 20. COMPOSITION OF FLY ASH
FROM THE BULL RUN PLANT
(August 1972)

Component	Weight percentage
Li_2O	0.04
Na_2O	0.23
K_2O	2.6
MgO	0.82
CaO	0.77
Al_2O_3	30.7
Fe_2O_3	6.8
SiO_2	53.2
TiO_2	1.9
P_2O_5	0.20

composition, as in the composition of the fly ash from Plant 6, is the lower percentage of calcium oxide compared with the percentages in ash from Western coals.

Sulfur-Dioxide Conversion Efficiency—

Institute personnel determined the efficiencies of conversion of sulfur dioxide to the trioxide at different flow rates of sulfur dioxide through the catalyst. The procedure for determining the efficiency of conversion at a given flow rate consisted of collecting the effluent sulfur trioxide in an air-cooled condenser and an impinger-bubbler filled with water and then collecting the residual sulfur dioxide in a bubbler filled with aqueous hydrogen peroxide. Both the sulfur trioxide and the sulfur dioxide were thus collected as sulfuric acid and determined in this form. Conversion efficiencies were approximately 80 and 70%, respectively, at the flow rates of sulfur dioxide produced with volume concentrations of 6.5 and 9.2% in the carrier stream of air flowing through the catalyst. Concentrations of sulfur trioxide thus introduced into the flue gas were calculated as 32 and 40 ppm at the estimated flow rate of the flue gas.

Precipitator Efficiency—

TVA personnel completed two determinations of the precipitator efficiency while sulfur trioxide was being injected and the plant was operating at full load. The results were 98.7% with 32 ppm of sulfur trioxide injected and 98.4% with 40 ppm injected. Several days later after the injection had been discontinued, another determination yielded essentially the same result, 98.6%.

There is a good deal of uncertainty about the value of the efficiency that would have been representative of the precipitator performance without conditioning. The value of 98.6% is suspect because of reports that the effects of sulfur trioxide conditioning may persist for several days after the injection is discontinued. The values estimated for full-load conditions on the basis of previous tests with low-sulfur coals[33] are of doubtful validity because, first, they were based on extrapolations of results for reduced-load conditions and, second, the extrapolations were made for a somewhat higher gas temperature, approximately 135°C rather than 125°C.

TVA's conclusion was that sulfur trioxide injection improved the efficiency of the precipitator significantly even though the degree of improvement was difficult to express quantitatively.[34] This conclusion was strengthened by the results obtained with the light-obscuration devices.

Fly-Ash Resistivity and Other Properties—

The results of determinations of fly-ash resistivity are given in Table 21. All of these data were obtained with the point-plane probe and with the electric field in the fly-ash samples near the breakdown level (between 10 and 20 kV/cm). The values of resistivity found with the unconditioned ash were all around 3×10^{10} ohm cm, and the values found with either 32 or 40 ppm of sulfur trioxide injected were approximately three orders of magnitude lower, around 3×10^{7} ohm cm.

Table 21. ELECTRICAL RESISTIVITY OF FLY ASH
AT THE BULL RUN PLANT
(August 1972)

Injected SO_3 concn, ppm	Resistivity,[a] ohm cm
0	4.4×10^{10}
	2.4×10^{10}
	1.2×10^{10}
	3.3×10^{10}
32	1.3×10^{7}
40	5.0×10^{7}
	3.0×10^{7}

[a] Temperature, about 125°C.

The resistivity data indicate that either of the concentrations of sulfur trioxide injected was excessive. The results obtained by TVA in later efficiency tests, it is understood, confirm this conclusion, indicating that the optimum concentration is nearer 20 ppm.

The results of analytical experiments with slurries of fly ash in water are given in Table 22. The samples of fly ash investigated in these experiments had been collected in alundum thimbles at the inlet and the outlet of the precipitator under isokinetic conditions. The pH data show that the unconditioned ash was acidic and the conditioned ash was even more acidic. The concentrations of sulfate dissolved from the ash show that marked increases in the amount of sulfate on the ash occurred as the result of conditioning. Comparison of data for samples from the inlet and outlet of the precipitator indicates that the samples from the outlet were more acidic and contained more sulfate than those from the inlet. This difference undoubtedly reflects the difference in surface area per unit of weight of ash at the two locations. The ash collected at the outlet was smaller in particle size and thus had a larger area-to-mass ratio.

Table 22. CHEMICAL PROPERTIES OF FLY ASH AT THE BULL RUN PLANT (AUGUST 1972)

Injected SO_3 concn, ppm	Sampling location	Ash properties[a]	
		pH	Sulfate, wt %
0	Precipitator inlet	4.3	0.53
	outlet	-[b]	-[b]
32	Precipitator inlet	3.9	2.24
	outlet	3.7	7.53
40	Precipitator inlet	4.0	2.60
	outlet	3.6	8.83

[a] For samples collected at a temperature of 125°C.

[b] Not determined because of the inadequate quantity of ash sampled.

Flue-Gas Concentrations—

Concentrations of sulfur oxides and water vapor in the flue gas at the inlet to the precipitator are listed in Table 23. The data in this table that are of the greatest interest are the concentrations of sulfur trioxide. The concentrations of

Table 23. CONCENTRATIONS OF FLUE GASES AT THE BULL RUN PLANT (AUGUST 1972)

Injected SO_3 concn, ppm	Concentrations[a]		
	SO_3, ppm	SO_2, ppm	H_2O, %
0	1.4	937	9.1
	1.5	774	9.2
	2.1	792	-
	1.3	846	-
32	15.8	983	9.2
	13.4	994	8.8
	11.2	1074	-
	9.2	1010	-
	9.0	974	-
	8.6	1010	-
40	11.0	855	9.5
	8.6	892	-

[a] For samples collected at the precipitator inlet at a temperature of 125°C.

sulfur trioxide found when there was no injection of the conditioning agent were around 1 to 2 ppm. The concentrations found when the conditioning agent was injected were higher but not exactly consistent with the rates of injection. On one occasion about 9 ppm was found when the injection rate was 32 ppm, and on another occasion about 13 ppm was found at the same injection rate. Approximately 10 ppm was found when the injection rate was increased to 40 ppm.

Obviously, a substantial fraction of the injected sulfur trioxide—one-fourth to one-third—was always found in the gas phase. However, the fraction remaining in the gas phase was lower than that at Plant 6, which had a fly ash of similar composition (see Tables 16 and 20). Probably the difference in the relative amounts of sulfur trioxide collected by the fly ash and allowed to remain in the gas phase was caused by the difference in temperature, which was lower at the Bull Run plant by about 35°C. Deposition of sulfur trioxide on the fly ash at the Bull Run plant could have been forced to go nearer to completion as the result of condensation with water vapor as sulfuric acid at the comparatively low flue-gas temperature. Deposition of sulfur trioxide on the fly ash at Plant 6 apparently occurred only as a result of an adsorption process.

Precipitator Electrical Data—

The configuration of the electrical sections in Collector 1B of the Bull Run plant is shown in Figure 4. The designation of the transformer-rectifier set supplying power to each section is also given in this figure.

TVA personnel maintained a detailed record of voltages and currents in all of the eight transformer-rectifier sets of the precipitator. The data compiled consisted of periodic readings of meters in the precipitator control room that registered primary voltages, primary currents, secondary currents, and spark rates. The data show that erratic variations occurred in each of these parameters on an hour-to-hour basis under all conditions of sulfur trioxide injection. They indicate that the circuitry intended to control the power supplies was unable to maintain constant values of any of the electrical parameters—voltage, current, or spark rate. Hence, the change in any one of these parameters as a result of a change in injection conditions was not always easy to discern. Even so, representative values of primary voltages, primary currents, and secondary currents in TR Sets 1LB and 1RB (powering electrical sections adjacent to the inlet of the precipitator) and in TR Sets 4LB and 4RB (for sections adjoining the outlet) are listed in Table 24. These values are described as "representative" inasmuch as each lies near the middle of the range of the recorded data.

The data in Table 24 indicate that the effects of sulfur trioxide injection were most clearly manifest by increases in the values of currents. However, the data show several anomalies, such as smaller increases in currents in all transformer-rectifier sets but TR Set 4RB when the concentration of injected sulfur trioxide was increased from 32 to 40 ppm.

One member of the TVA staff used auxiliary instrumentation to record secondary current *versus* secondary voltage in several of the power supplies with and without sulfur trioxide injection. The data for an inlet and an outlet set, TR Sets 1LB and 4LB, are shown by the graphs in Figure 5. The curves in this figure portray the variations that occurred in current density (the ratio of measured current to known electrode area) as manual adjustments were made to alter voltage. The location of the upper terminus of each curve indicates the current density and voltage maintained with the power supplies under automatic control. For each of the curves plotted for experiments without conditioning, the change in slope to a negative value corresponds to the onset of moderate to heavy sparking. The absence of a change in slope for each of the other two curves indicates that sparking was suppressed during conditioning.

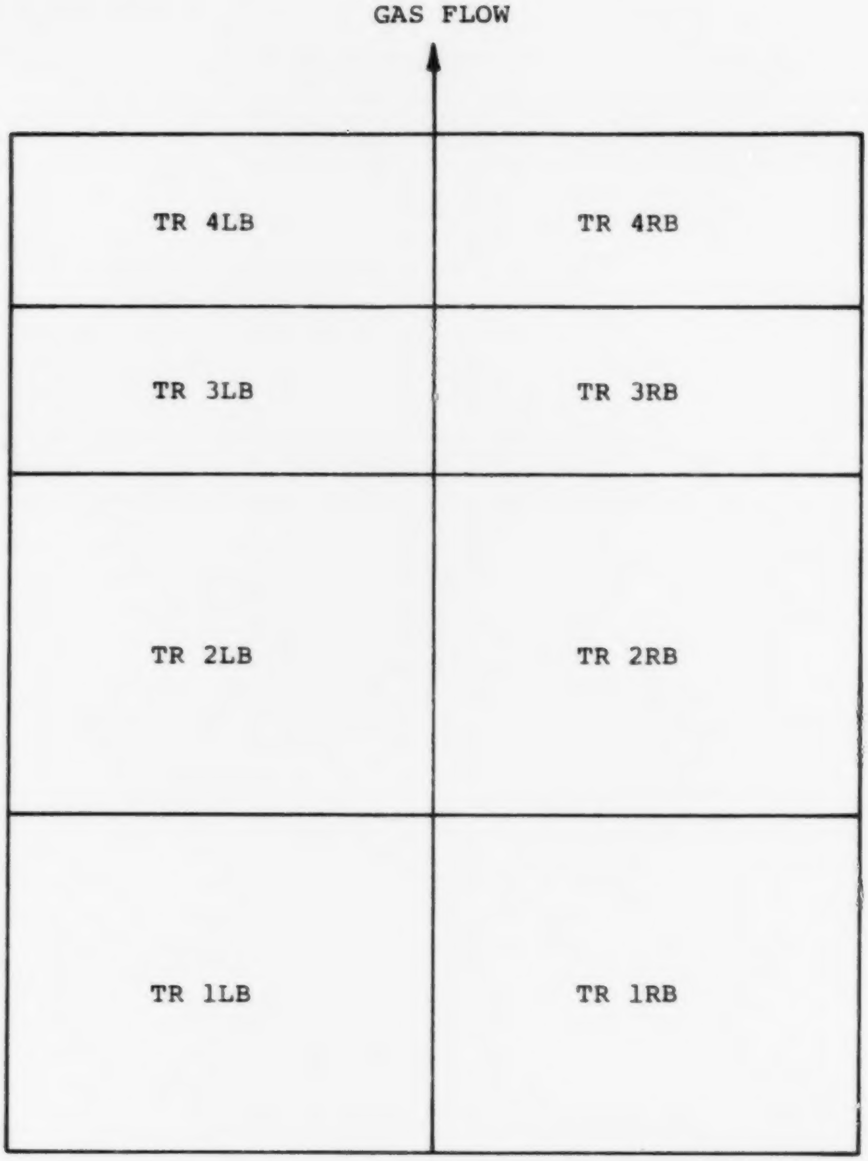
GAS FLOW
TR 4LB
TR 4RB
TR 3LB
TR 3RB
TR 2LB
TR 2RB
TR 1LB
TR 1RB

Figure 4. Schematic diagram of electrical sections in Collector 1B at the Bull Run plant

Table 24. PRECIPITATOR ELECTRICAL DATA FROM THE BULL RUN PLANT (AUGUST 1972)

TR Set[a]	Injected SO_3 concn, ppm	Primary voltage, V	Primary current, A	Secondary current, mA
1LB	0	310	59	350
	32	315	72	420
	40	310	65	380
1RB	0	320	69	365
	32	350	75	445
	40	320	62	405
4LB	0	345	34	330[b]
	32	330	40	370[b]
	40	350	37	380[b]
4RB	0	385	53	340
	32	420	68	430
	40	425	74	465

[a] Locations of the electrical sections powered by these transformer-rectifier sets are shown in Figure 4.

[b] The recorded values were only one-half of those listed. However, because one of the two bushings was grounded and only one-half of the electrode area was in service, the recorded values were doubled to permit a comparison with those following for TR Set 4RB.

The current-voltage data shown in Figure 5 are qualitatively and also semiquantitatively consistent with the observed decrease in resistivity that was produced with sulfur trioxide injection. To interpret the data in a quantitative sense, consider the shift in voltage at a current density of 10 nA/cm^2 for TR Set 1LB with the conditioning agent added: about 2 kV to the left along the voltage axis. Furthermore, assume that the thickness of fly ash deposited on the electrodes energized by this set was the same for both conditioned and unconditioned ash. The thickness of the fly-ash deposit can then be calculated from the equation:

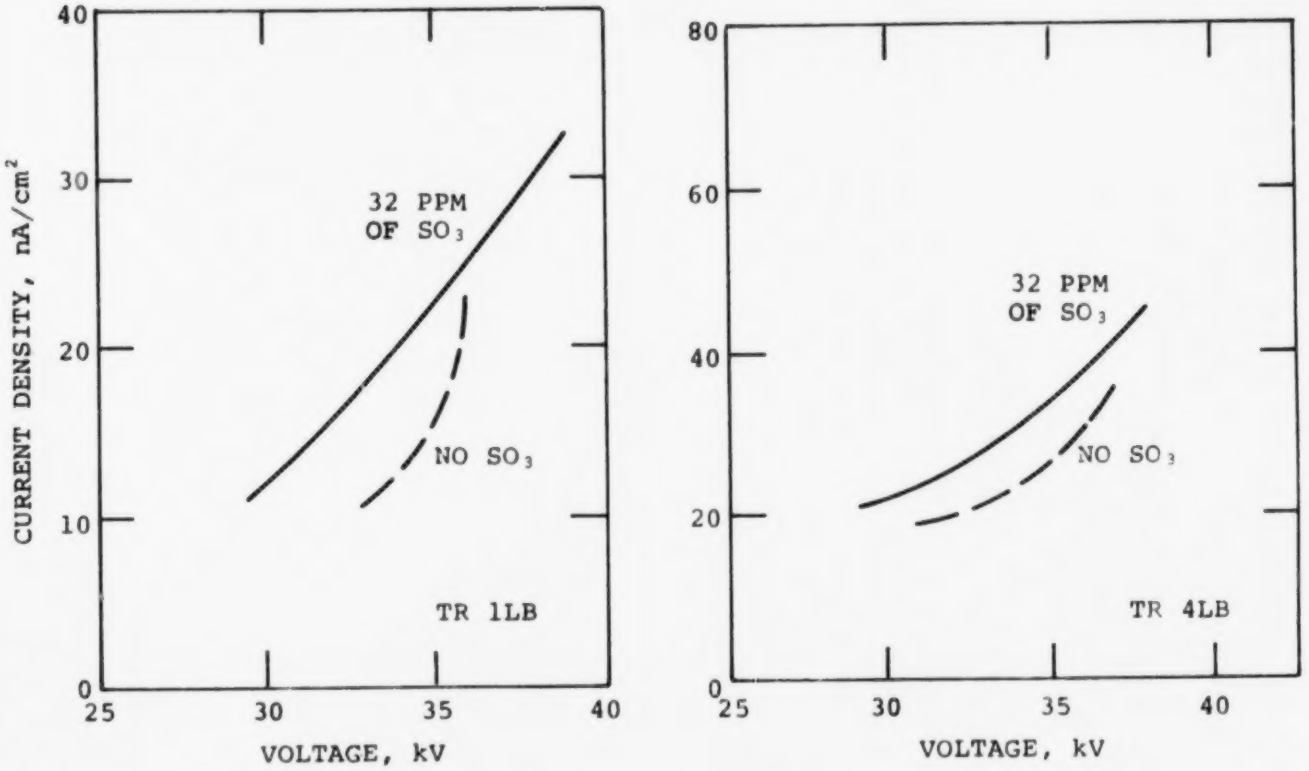

Figure 5. Current density *versus* voltage in Collector 1B of the Bull Run plant (August 1972)

$$t = \Delta V/j(\rho_u - \rho_c)$$

where t = thickness (cm)

ΔV = voltage shift (2×10^3 V)

j = current density (10×10^{-9} A/cm^2)

ρ_u = resistivity of unconditioned ash (ca. 3×10^{10} ohm cm)

ρ_c = resistivity of conditioned ash (ca. 3×10^7 ohm cm)

Solving the equation yields $t = 6.7$ cm. At first glance, this appears to be an absurdly high value compared with the wire-to-plate spacing of 11.4 cm. However, if the probable lack of uniformity in current density and the possible errors in the resistivity values are taken into account, the calculated thickness does not appear unreasonably large.

Results of the Second Investigation (1974)

The second investigation of conditioning at the Bull Run plant was carried out during July of 1974. The enlarged conditioning system treating the fly ash entering all four precipitators was in operation at that time; however, as during the preceding investigation in 1972, all of the experimental work was concerned with the precipitator referred to as Collector 1B.

There were two purposes of the second investigation at the Bull Run plant. One objective was to determine the extent of rapping reentrainment with variations in the electrical resistivity of the ash (adjusted by use of the conditioning system) and with variations in some of the rapping parameters (interval between rapping events, power used to actuate the vibratory rappers, and duration of the rapper vibrations). The second objective was to determine the change in the resistivity of the ash produced with sulfur-trioxide injection at a lower level than before (around 15 ppm instead of 32 to 40 ppm) and make a comprehensive study of the distribution of the injected sulfur trioxide between the flue gas and the fly ash entering and leaving the precipitator. Attainment of both experimental objectives was aided by TVA personnel. Members of the TVA staff determined ash concentrations at the inlet and the outlet of the precipitator to be used in calculations of precipitator efficiencies; they also recorded electrical data for various sections of the precipitator. The results of the studies dealing primarily with rapping reentrainment will be presented in a separate report that is to be submitted to TVA; the results of the studies more directly concerned with the conditioning process are given in this report.

Coal and Fly-Ash Compositions—

Coal from an unspecified source was burned as a fuel during the two weeks of the investigation carried out in July of 1974. The sulfur content of this fuel proved to be quite consistent throughout this period, averaging 0.82% by weight with minimum and maximum values of 0.74 and 0.95%. Analytical data obtained by TVA for 19 samples of coal collected during the two-week period are shown by the following averages from individual analyses:

Sulfur, 0.8%
Ash, 15.9%
Moisture, 7.5%
Heat value, 6,200 cal/g
(11,100 Btu/lb)

Samples of fly ash collected on four occasions with alundum thimbles at the inlet of the precipitator were analyzed to determine their overall compositions. Two of the samples analyzed were collected during the first week of the investigation when there was no injection of sulfur trioxide. The other two samples were collected during the second week when sulfur trioxide was injected to produce an approximate concentration of 15 ppm. Each analysis showed approximately the same composition, which is indicated by the average weight percentages of the several constituents that are given in Table 25. The composition was very similar to that found during the 1972 investigation (Table 20).

Sulfur-Dioxide Conversion Efficiency—

As indicated in the previous paragraph, the investigation during the first week was carried out without any injection of sulfur trioxide, whereas the investigation during the second week was carried out with the conditioning agent injected to produce a concentration of about 15 ppm in the flue gas. This approximate value of the concentration was obtained by regulating the flow rate of sulfur dioxide to the converter, as indicated by a calibrated monometer. It was assumed that about 80% of the sulfur dioxide would be converted to the trioxide and that the normal flow rate of flue gas to the precipitator would dilute the sulfur trioxide to the concentration desired.

Table 25. COMPOSITION OF FLY ASH
FROM THE BULL RUN PLANT
(July 1974)

Component	Weight percentage
Li_2O	0.07
Na_2O	0.27
K_2O	2.7
MgO	0.76
CaO	0.38
Al_2O_3	29.8
Fe_2O_3	3.9
SiO_2	52.7
TiO_2	1.88
P_2O_5	0.18
Volatiles	7.1

To permit a more accurate estimate of the injected concentration of the conditioning agent, the actual efficiency of the conversion of sulfur dioxide was determined experimentally. The result of the determination confirmed that the conversion efficiency was about 80%. Other analytical information indicated that at the selected flow rates of sulfur dioxide and dilution air to the converter the concentration of sulfur dioxide entering the converter was 4.4% by volume.

Determinations of the flow rate of flue gas at the outlet of the precipitator (a part of the study of the efficiency of the precipitator) showed that the flow rate was somewhat higher than the value originally estimated. Thus, although the efficiency of conversion of sulfur dioxide to the trioxide was the expected value, the calculated concentration of sulfur trioxide injected was somewhat lower than the intended value—about 14 ppm rather than 15 ppm.

Precipitator Efficiency—

During the first week of the investigation, TVA personnel made a series of determinations of the precipitator efficiency without sulfur-trioxide injection but with several changes in rapping parameters. During the second week, another series of determinations was made with sulfur-trioxide injection and with changes in rapping parameters that were similar to those made during the first week. Data from the efficiency determinations are summarized in Table 26. The information included in this table consists of the concentration of SO_3 used for treating the fly ash, the conditions under which the

Table 26. PRECIPITATOR EFFICIENCIES AT THE BULL RUN PLANT (JULY 1974)

Injected SO_3 concn, ppm	Test	Rapping[a] Interval	Rapping[a] Power	Rapping[a] Duration	Inlet ash concn, g/m^3 (gr/ft^3)	Efficiency, %
0	2E	N	N	N	17.1 (7.43)	69.7
	5E	2N	N	N	16.5 (7.19)	78.4
	8E	N	N/2	N	20.4 (8.85)	75.0
	12E	2N	N/2	N	18.0 (7.81)	77.4
	10E	-	No rapping	-	19.6 (8.53)	82.0
14	14E	N	N	N	17.0 (7.39)	93.5
	23E	2N	N	N	17.2 (7.48)	97.4
	27E	2N	N	N/6	20.0 (8.69)	92.0
	28E	2N	N/2	N/6	19.3 (8.37)	92.4
	16E	-	No rapping	-	16.0 (6.97)	96.8

[a] N indicates normal interval, power, or duration. Multipliers and divisors of N designate how the intensity of rapping was reduced.

rappers were operated, the observed concentration of fly ash at the inlet of the precipitator, and the calculated efficiency of ash collection.

With no injection of sulfur trioxide and with the rappers operating normally, the observed efficiency was surprisingly low, only 69.7%, compared with efficiencies determined several years earlier. With 14 ppm of sulfur trioxide injected and the rappers again operating normally, the efficiency increased to 93.5% but it was still below the level found in 1972 with higher concentrations of the conditioning agent (see p. 46).

The effects of changes in rapping conditions on precipitator efficiency will be discussed in detail in another report. However, in connection with the role of sulfur trioxide as a conditioning agent, it is noteworthy that extending the interval between rapping events, reducing the intensity of rapper vibrations, or discontinuing rapping altogether caused a significant improvement in efficiency in the absence of conditioning. On the other hand, it is evident that none of the changes in rapping conditions caused a comparable relative improvement in efficiency when sulfur trioxide was used for conditioning the fly ash. At least part of the effectiveness of sulfur-trioxide conditioning appears attributable, therefore, to a suppression of rapping losses of collected ash.

In further consideration of the role of sulfur trioxide as a conditioning agent, it is of interest to analyze data showing how the efficiency of fly-ash collection varied across the precipitator as an apparent result of the gradient in temperature. The data in Table 27 are from four representative efficiency tests in which efficiency values were calculated for each of the four sampling ports at the precipitator outlet. Here, the flue-gas temperature ranged from 112 to 135°C. This temperature gradient was similar to that at the precipitator inlet and was caused by the Ljungstrom air preheater upstream from the precipitator. In two tests without injection of sulfur trioxide, there was no clear-cut relationship between efficiency and gas temperature. In two tests with injection of sulfur trioxide, on the other hand, there was a strong indication of decreasing efficiency with increasing temperature. It is reasonable to conclude that this relationship is the result of decreasing uptake of the sulfur trioxide by the ash with increasing gas temperature. This conclusion is supported by the results of fly-ash gas analyses given later in this report.

Table 27. PRECIPITATION EFFICIENCY AS A FUNCTION OF GAS TEMPERATURE AT THE BULL RUN PLANT (JULY 1974)

Injected SO_3 concn, ppm	Test	Rapping	Efficiency, %,[a] *vs.* outlet gas temp 112°C	120°C	130°C	135°C
0	2E	Normal	71.4	75.3	64.8	67.7
	10E	None	81.9	85.4	78.6	82.7
15	14E	Normal	96.9	95.5	91.8	90.7
	16E	None	97.6	97.8	96.8	95.0

[a] Calculated by use of the average concentration of fly ash entering the precipitator.

Indirect indications of dust concentrations evolved from the precipitator were obtained on a continuous basis with a Lear-Siegler instrument for determining the opacity of the gas stream at the outlet of the precipitator. The light-obscuration data recorded with this device are of interest in several respects. The recorder-pen fluctuations were greatly suppressed during sulfur trioxide injection, indicating that the quantity of ash reentrained during rapping events was suppressed as a result of conditioning. The range of pen locations was shifted significantly downscale by injection, showing that there was a significant reduction in the time-average concentration of ash evolved from the precipitator as well as a reduction in the concentration immediately following each rapping event. The rate of pen response as the rate of injection of sulfur trioxide was altered indicated that both short- and long-term changes occurred in the ash concentration. When injection was started, for example, the pen quickly began to move downscale, but the shift in its location and the reduction in its oscillations continued over a period of several hours.

Fly-Ash Resistivity—

The point-plane resistivity probe was inserted into one of the sampling ports at the inlet precipitator where the gas temperature was near the mean value (about 125°C) and used to determine the electrical resistivity of the fly ash with and without conditioning. The results of two series of determinations of resistivity at electric fields near the breakdown strength of the collected ash are given in Table 28. The resistivity of unconditioned ash was approximately 2×10^{10} ohm cm, and the value for ash conditioned with sulfur trioxide was significantly lower as expected, approximately 3×10^{9} ohm cm. These data may be compared with the results obtained during the earlier investigation at the Bull Run plant (page 47). For unconditioned ash, the resistivity values were essentially the same in both investigations. For conditioned ash, the resistivity value with 14 ppm of sulfur trioxide injected was approximately two orders of magnitude higher than the values found previously with 32 or 40 ppm of the conditioning agent injected. Comparison of the resistivity from the studies on separate occasions appears justified on the basis of the similarity of the compositions of the fly ash (Tables 20 and 25).

Table 28. ELECTRICAL RESISTIVITY OF FLY ASH AT THE BULL RUN PLANT (JULY 1974)

Injected SO_3 concn, ppm	Resistivity,[a] ohm cm
0	1.2×10^{10}
	1.1×10^{10}
	3.2×10^{10}
14	3.1×10^{9}
	4.0×10^{9}
	3.2×10^{9}

[a] Temperature, about 125°C.

Fly-Ash Properties in Aqueous Slurries—

Values of the equilibrium pH and the weight percentage of soluble sulfate were determined for a series of fly-ash samples from two sources: (1) alundum thimbles used at the inlet of the precipitator for the efficiency tests and (2) hoppers under the precipitator receiving the ash that was removed from the gas stream during the efficiency tests.

Samples collected in thimbles from each of the sampling ports during one test without sulfur trioxide injection and during a second test with injection were analyzed individually. The results of the analyses are given in Table 29. Other information in this table consists of the flue-gas temperatures at which the samples were collected. The analytical data for the unconditioned ash show no systematic variation of either pH or sulfate concentration with sampling temperature or location (inlet or outlet of the precipitator). The data for the conditioned ash, on the other hand, show consistently lower pH values and higher sulfate concentrations at the outlet compared with the inlet. Moreover, the sulfate concentrations for the conditioned ash from the outlet show a marked decrease as a result of an increase in temperature.

Table 29. CHEMICAL PROPERTIES OF INDIVIDUAL SAMPLES OF FLY ASH COLLECTED IN THIMBLES AT THE BULL RUN PLANT (JULY 1974)

Injected SO_3 concn, ppm	Test	Inlet samples			Outlet samples		
		Temp, °C	pH	Sulfate, wt %	Temp, °C	pH	Sulfate, wt %
0	2E	116	4.9	0.29	112	5.0	0.26
		122	5.1	0.22	121	4.9	0.22
		126	4.8	0.29	130	4.8	0.29
		137	5.0	0.26	135	4.8	0.29
14	14E	112	4.5	0.47	112	4.2	1.97
		122	4.5	0.44	121	4.2	1.68
		126	4.5	0.47	130	4.2	1.35
		136	4.5	0.44	135	4.2	1.35

Analytical data for composites of samples collected in thimbles from several efficiency tests with and without conditioning are given in Table 30. Information included in this table are calculated concentrations of sulfur trioxide in the gas phase that are equivalent to the concentrations of sulfate in

Table 30. CHEMICAL PROPERTIES OF COMPOSITE SAMPLES OF FLY ASH COLLECTED IN THIMBLES AT THE BULL RUN PLANT (JULY 1974)

		Inlet samples[a]			Outlet samples[a]		
Injected SO_3 concn, ppm	Test	pH	Sulfate, wt %	Equiv SO_3,[b] ppm	pH	Sulfate, wt %	Equiv SO_3,[b] ppm
0	2E	5.0	0.26	10.4	4.9	0.28	3.3
	5E	4.3	0.44	16.9	4.8	0.33	2.7
	8E	4.7	0.22	10.4	4.8	0.33	3.9
	12E	4.8	0.22	11.5	4.8	0.22	2.6
14	14E	4.5	0.46	18.0	4.2	1.49	3.7
	23E	4.3	0.58	23.2	4.1	2.02	2.3
	27E	4.4	0.51	23.7	4.1	1.47	5.9

[a] Composite samples for a mean gas temperature of about 125°C.

[b] Calculated as the concentration of SO_3 in the gas phase that would be equivalent to the concentration of sulfate in the ash.

the ash. Calculations of these hypothetical concentrations of sulfur trioxide in the gas phase were made by use of the observed concentrations of sulfate in the ash and the experimentally determined concentrations of fly ash at the inlet and outlet of the precipitator. In general, the data in Table 30 indicate the following:

- pH was lowered substantially by the injection of sulfur trioxide, particularly for outlet samples.

- Sulfate concentrations were increased markedly by the injection of sulfur trioxide, again especially for outlet samples.

- Sulfur trioxide concentrations in the gas phase equivalent to sulfate concentrations in the ash were much higher for samples at the inlet during injection of the conditioning agent. Thus, they reflect the expected removal of at least part of the injected agent from the gas stream by the ash.

- Sulfur trioxide concentrations calculated for outlet samples do not show much change as a result of sulfur trioxide injection. The lower concentrations of ash at the outlet during injection offset the higher concentrations of sulfate in the ash.

Analytical data given in Table 30 for the inlet sample from Test 5E are anomalous. The data indicate much more uptake of sulfur trioxide than the data for other samples collected without conditioning. The first analysis of the sample was repeated to determine whether a serious experimental error had been made; evidently, there was no significant error. Perhaps the inlet samples for Test 5E were incorrectly labeled; the samples analyzed may have been from another test that was carried out during sulfur trioxide injection.

The results of analyses of composites of the hopper samples are given in Table 31. The concentrations of sulfur trioxide in this table are based on the observed concentrations of sulfate in the ash and the calculated concentrations of ash that were precipitated and deposited in the hoppers. The latter values were calculated from the observed concentrations of ash entering the precipitator and the experimentally determined efficiencies of precipitation. All of the data in Table 31 reflect a marked increase in the collection of sulfur trioxide by the ash during the injection of this compound.

Table 31. CHEMICAL PROPERTIES OF COMPOSITE SAMPLES OF FLY ASH FROM PRECIPITATOR HOPPERS AT THE BULL RUN PLANT (JULY 1974)

Injected SO_3 concn, ppm	Test	pH	Sulfate, wt %	Equiv SO_3,[a] ppm
0	2E	5.1	0.16	4.4
	5E	5.0	0.19	5.7
	8E	5.1	0.15	5.3
	12E	5.0	0.19	7.7
14	14E	4.5	0.31	11.4
	23E	4.5	0.39	14.7
	27E	4.5	0.43	19.4

[a] Calculated as the concentration of SO_3 in the gas phase that would be equivalent to the concentration of sulfate in the ash.

Data from Tables 30 and 31 are combined in Table 32 to permit a comparison of the analytical results with the mass conservation relationship expressed as follows:

> The combined quantities of sulfate in ash from outlet thimbles and precipitator hoppers should be equal to the quantity of sulfate in ash from inlet thimbles.

Table 32. CONCENTRATIONS OF SULFUR TRIOXIDE EQUIVALENT TO THE CONCENTRATIONS OF SULFATE IN FLY ASH AT THE BULL RUN PLANT (JULY 1974)

Injected SO_3 concn, ppm	Test	Equiv SO_3 concn, ppm			
		Thimble samples		Hopper samples	Difference[a]
		Inlet	Outlet		
0	2E	10.4	3.3	4.4	2.7
	8E	10.4	3.9	5.3	1.2
	12E	11.5	2.6	7.7	1.2
	(av)	10.8	3.3	5.8	1.7
14	14E	18.0	3.7	11.4	2.9
	23E	23.2	2.3	14.7	6.2
	27E	23.7	5.9	19.4	-1.6
	(av)	21.6	4.0	15.2	2.5

[a] Calculated by subtracting the sum of the outlet and thimble samples from the value for the inlet sample.

A test of this relationship is provided by the concentrations of sulfur trioxide equivalent to the quantities of sulfate in the ash, as summarized in Table 32. If the relationship were satisfied by the experimental data, all of the values in the last column of the table would be zero. Obviously, the relationship is not satisfied precisely. Even so, the precision in the analytical data appears to be generally acceptable, especially when examined in terms of the averages in sulfur trioxide concentrations. Average values of the difference in sulfate found in the inlet samples and in the combination of outlet and hopper samples represents 10 to 20% of that found in the inlet samples. A possible explanation for the discrepancy in the results is that in collecting fly ash in alundum thimbles part of the sulfur trioxide actually present in the gas phase within the flue-gas duct is deposited on the collected ash. This source of error would probably be more significant at the inlet of the precipitator than at the outlet because of the greater quantity of ash collected.

The data in Table 32 permit estimates to be made of the quantity of the injected sulfur trioxide that was collected by the fly ash. Based on the differences in the average calculated concentrations of sulfur trioxide deposited on the ash with and without injection, the estimates are as follows:

- Inlet samples—(21.6-10.8) = 10.8 ppm
- Outlet and hopper samples—(19.2-9.1) = 10.0 ppm

The first value represents 77% of the injected sulfur trioxide; the second value represents 72% of the total.

Flue-Gas Concentrations—

Concentrations of sulfur trioxide, sulfur dioxide, and water vapor in the flue gas at the inlet and the outlet of the precipitator were determined at several sampling ports at each location. As discussed in the following paragraph, the concentration of sulfur trioxide depended upon where the sampling port was located in either of the sampling planes; as expected, it also depended on whether sulfur trioxide was being injected to condition the fly ash. The concentrations of sulfur dioxide and water, on the ohter hand, were essentially independent of these factors; they appeared to vary randomly about average values of 708 ppm and 9.8% by volume, respectively.

The observed concentrations of sulfur trioxide at the inlet and the outlet of the precipitator are plotted in Figure 6 as functions of the sampling locations, expressed as fractions of the distance across the gas stream from one vertical wall of each duct to the opposite wall. Curves portraying the temperature profiles across the two ducts are also plotted in the figure. The concentrations of sulfur trioxide found both with and without injection obviously decreased as the gas temperature decreased; thus, concentration profiles are shown by curves that are, in general, parallel to the temperature profiles. (In the lower range of gas temperatures, the concentrations of sulfur trioxide without injection were less than 1 ppm and thus were too low for reliable determination; in the graph, these concentrations are arbitrarily plotted as 0.5 ppm.)

Areas under the curves portraying the concentrations of sulfur trioxide indicate that the average concentrations of sulfur trioxide were as follows:

Without injection—
Inlet, 1.2 ppm
Outlet, 1.0 ppm

With injection—
Inlet, 5.8 ppm
Outlet, 5.6 ppm

The apparent differences between inlet and outlet concentrations with or without injection are not large enough to represent real differences. Thus, it is reasonable to conclude that the concentration of sulfur trioxide was essentially the same on both sides of the precipitator (about 1 ppm

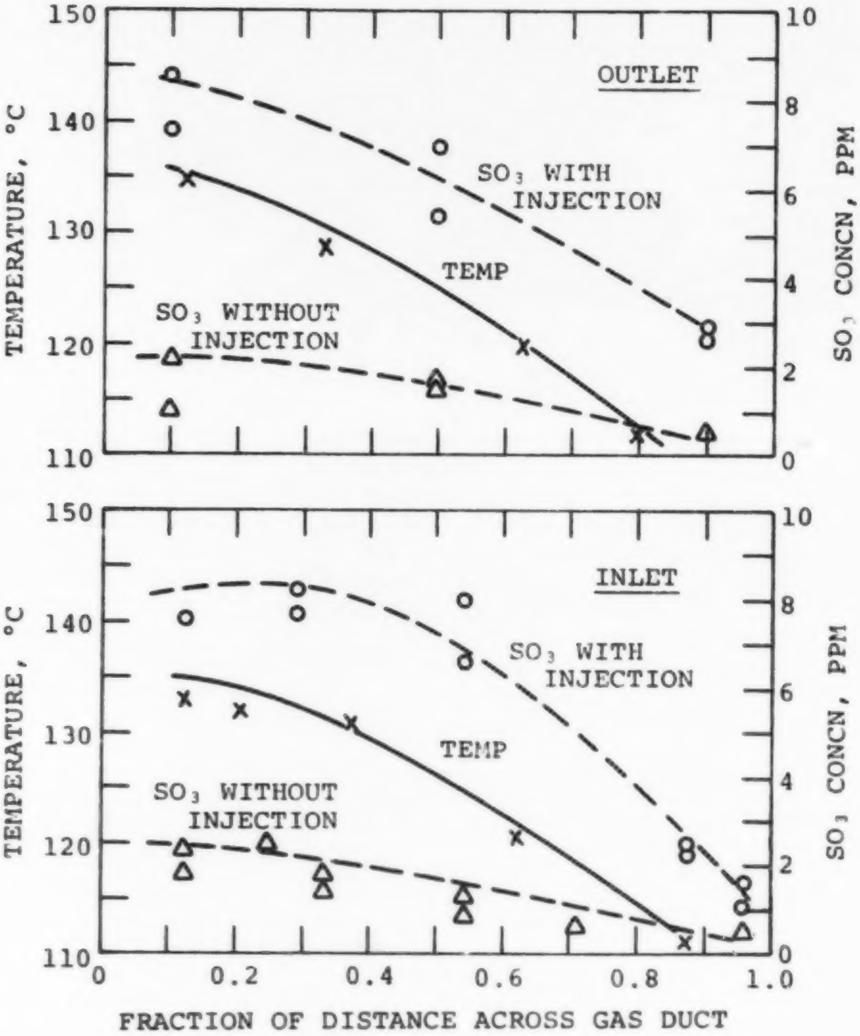

Figure 6. Concentration of sulfur trioxide as a function of gas temperature at the Bull Run plant (July 1974)

without injection or about 6 ppm with injection) and that the concentration in either location was increased by essentially the same amount as a result of injection (about 5 ppm). The concentration of sulfur trioxide not collected by the fly ash and thus allowed to pass from the precipitator to the stack and thence to the atmosphere represents about 36% of the concentration injected upstream from the precipitator (calculated as 14 ppm).

Analyses of fly ash discussed previously in this report indicate that 10 to 11 ppm of the injected sulfur trioxide was collected by the fly ash. Thus, combined analyses of the ash and the gas accounted for 15 to 16 ppm of injected sulfur trioxide, slightly in excess of the 14 ppm calculated as the total concentration injected. The discrepancy seems gratifyingly small in view of the numerous potential sources of analytical error.

Precipitator Electrical Data—

Electrical data for the power supplies of the precipitator under automatic control are compiled in Table 33. The data consist of values of primary voltage, primary current, secondary current, and spark rate; the data were computed by averaging meter readings during a series of efficiency tests, first without sulfur trioxide injection and then with injection. With a few exceptions, the injection of sulfur trioxide increased voltages and currents and decreased the spark rate. These changes are all consistent with the observed decrease in fly-ash resistivity, but they are not necessarily indicative of this effect alone as discussed below.

Electrical data obtained with the power supplies under manual control and with the primary voltage thus variable are shown in Figure 7. Here, the data show current densities (calculated from recorded values of secondary current) as functions of secondary voltage in an inlet and an outlet electrical field of the precipitator. The segments of the curves with positive slopes portray the data obtained with no sparking or very light sparking; the segments with negative slopes in regions of high current density represent the experimental results with moderate to heavy sparking. The short horizontal lines intersecting each curve indicate the average values of current density observed with the power supplies under automatic control (calculated from the values of secondary current given in Table 33).

The aspect of the data in Figure 7 that appears to be of major significance is the indication that the injection of sulfur trioxide permitted both higher current densities and higher voltages to be reached without the occurrence of excessive sparking, with the reason being some effect other than

Table 33. PRECIPITATOR ELECTRICAL DATA FROM THE BULL RUN PLANT (JULY 1974)

TR Set	Injected SO_3 concn, ppm	Primary voltage, V	Primary current, A	Secondary current, mA	Sparks per min
1LB	0	215	16	150	230
	14	285	32	165	105
1RB	0	175	14	160	265
	14	225	16	140	150
2LB	0	250	22	150	180
	14	320	37	210	150
2RB	0	275	33	200	120
	14	335	29	175	60
3LB	0	285	19	110	210
	14	325	23	130	150
3RB	0	320	30	145	140
	14	385	34	165	80
4LB	0	260	13	100	220
	14	300	17	110	165
4RB	0	280	15	120	270
	14	360	17	105	70

the observed lowering of fly-ash resistivity. The shifts in the current-voltage curves were to the right along the voltage axis, whereas shifts to the left would conform to the lowering of resistivity as the only effect of the conditioning process. Shifts in the voltage curves to the right along the voltage axis at least suggest the possibility of a space-charge effect resulting from the introduction of less mobile charge carriers in the gas stream. One possibility is that the added concentration of sulfur trioxide (or the vapor of sulfuric acid) assumed most of the ionic space charge and the new ions thus introduced carried current with a lower mobility than the normally occurring ions produced from oxygen, water vapor, and sulfur dioxide. An alternative possibility is that part of the added sulfur trioxide was condensed as a fine mist of sulfuric acid and then electrically charged, causing a very pronounced shift in charge carriers from gaseous ions to relatively immobile acid particles.

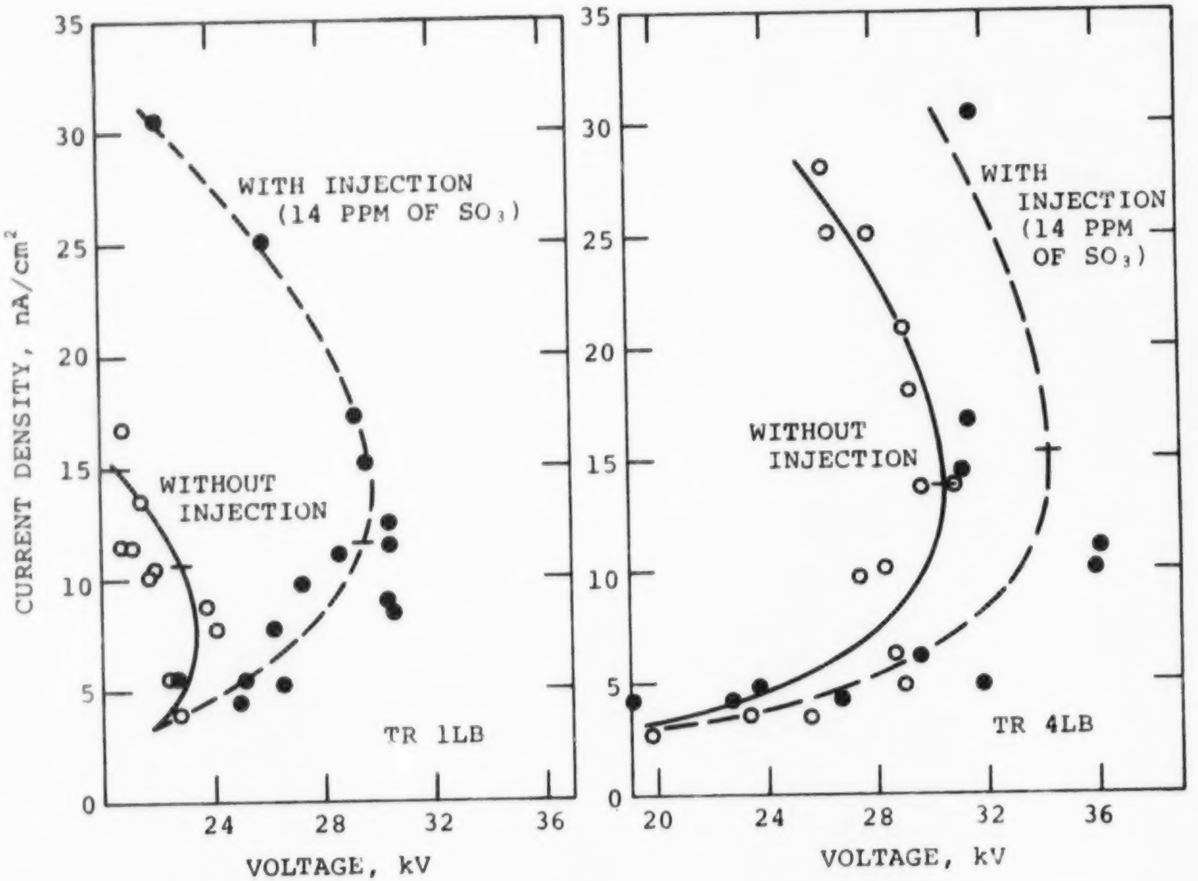

Figure 7. Current density *versus* voltage in Collector 1B of the Bull Run plant (July 1974)

There is a decided contrast between the effects of sulfur-trioxide injection at the Bull Run plant during the first investigation in 1972 and the later investigation in 1974 (compare Figures 5 and 7). During the first investigation, sulfur trioxide injection caused a shift in the current-voltage curves to the left on the voltage axis in a manner consistent with a decrease in resistivity. During the second investigation, the shift observed was to the right for different reasons such as the one described above. Another difference between the results of the two investigations was that sparking required much higher current densities and voltages in the first investigation than in the second. A possible explanation for this difference is that the alignment of the corona wires and collection electrodes deteriorated significantly during the time between the two investigations.

SECTION VI

RESULTS OF STUDIES OF CONDITIONING WITH AMMONIA

The studies of conditioning with ammonia in TVA power plants are classified in the following discussion as to the sulfur content of the coal from which the fly ash originated. In two power plants, ammonia was investigated as a conditioning agent for ash from low-sulfur coals. Furthermore, in one of these two plants and in a third plant, ammonia was investigated as a conditioning agent for ash from high-sulfur coals, as in the original study of Reese and Greco.[5] Both types of coal were from the Eastern mines that supply the TVA system.

The fly ash produced by the low-sulfur coals differed significantly from the ash evolved from the low-sulfur Western coals that were involved in several of the studies of sulfur trioxide conditioning discussed in Section V of this report; the ash was more similar to that from the low-sulfur Eastern coals burned during the studies of sulfur trioxide at Plant 6 and at TVA's Bull Run plant. The major differences in ash properties were lower electrical resistivities and lower calcium-oxide contents (and hence lower basicities). Associated with these differences in ash properties were higher naturally produced concentrations of sulfur trioxide in the flue gas compared with the concentrations produced from low-sulfur Western coals.

It might be expected that ammonia conditioning would occur by substantially different mechanisms with the fly ash from low- and high-sulfur coals. However, the nature of the combustion products described above for the low-sulfur coals led to the occurrence of similar conditioning phenomena with ash from both low- and high-sulfur coals.

POWER PLANTS BURNING LOW-SULFUR COALS

Although TVA's initial experience with ammonia conditioning had only involved fly ash from high-sulfur coal, the utility undertook an evaluation of ammonia conditioning of ash from low-sulfur coals during 1972. The first investigation with a low-sulfur coal was made at the Widows Creek plant, where Reese and Greco's original investigation had been carried out.[5] The second investigation was made at the Bull Run plant shortly after the initial trials of sulfur trioxide conditioning were started at this plant (described in Section V).

Widows Creek Plant, Unit 7

During brief occasions during June and July of 1972, low-sulfur coal instead of the usual high-sulfur coal was burned on a trial basis at the Widows Creek plant in Unit 7 (550 MW). In some of the experimental work, no ammonia was used. In comparative experiments, however, ammonia injection downstream from the air preheater was used to condition the ash. (Originally, ammonia was injected upstream from the air preheater;[5] however, problems with preheater pluggage necessitated relocation of the injection manifold.)

TVA personnel determined the precipitation efficiency of fly-ash collection with and without conditioning. They also investigated the electrical behavior of the precipitator with and without conditioning. Members of the Institute staff obtained data on the properties of the fly ash and the flue gas. The first experiments were conducted during June with the precipitator designated as Collector 7A, but they were discontinued before completion because of a boiler-tube leak. The later more extensive experiments were conducted during July with one of the other precipitators of identical design, Collector 7B.

Coal and Fly-Ash Compositions—

The results of coal analyses for the experiments in June and July were very similar. The following data are representative of the coal burned during the two series of experiments:

Sulfur,	0.9%
Ash,	17.6%
Moisture,	5.4%
Heat value,	6,400 cal/g (11,600 Btu/lb)

The results of a comprehensive analysis of the fly ash (collected in an alundum thimble at the inlet of Collector 7B) are given in Table 34. This analysis indicates that the material followed the usual pattern of fly ash from Eastern coals in containing little calcium oxide.

Table 34. COMPOSITION OF FLY ASH FROM A LOW-SULFUR COAL AT WIDOWS CREEK UNIT 7 (June-July 1972)

Component	Weight percentage
Li_2O	0.09
Na_2O	0.21
K_2O	3.2
MgO	1.3
CaO	0.79
Al_2O_3	30.2
Fe_2O_3	6.0
SiO_2	54.2
TiO_2	1.3
P_2O_5	0.60
SO_3	0.29

Precipitator Efficiencies—

Two experiments at Collector 7B with and without ammonia present as a conditioning agent yielded efficiency data that were considered reliable by the supervisor of the TVA research team. One of these experiments was carried out with a gas temperature of 143°C; the efficiencies calculated from inlet and outlet fly-ash concentrations were 93.9% with no ammonia injection and 98.5% with 13 ppm of ammonia injected. The second experiment showed an even greater improvement in efficiency at 132°C; the efficiency increased from 89.9% to 98.3% with 10 ppm of ammonia injected.[35]

A Bailey bolometer equipped with a recorder provided a real-time record of the changes in the concentration of fly ash emitted from the precipitator. Usually, the recorder responded rapidly to changes in the rate of ammonia injection. The recording for one day of experimentation yielded the following results:

- No ammonia injection. The pen fluctuated rapidly and irregularly between scale positions of approximately 22 and 48 on a range of 100.

- Ammonia injected for roughly 20 min intervals, first at approximately 7.5 ppm and later at approximately 10.0 ppm. Injection at the lower concentration caused a rapid change in oscillation of the pen, lowering the range of scale positions from 22-48 to 20-38 and regulating the time interval between the high values (appearing as spikes) to about 5 min. Subsequent injection at the higher concentration caused further suppression of the range of scale positions to 20-30.

- Ammonia injected for several hours with the concentration increased from 10.0 to 13.1 ppm. The main effect was further suppression of the range in pen positions to 20-24.
- Ammonia injection discontinued. A rapid return of the pen oscillation to the range and frequency first noted was observed.

Close observation of the pen movement giving the spikes spaced at 5-min intervals during ammonia injection showed that approximately five surges in pen location produced each of the spikes evident on the slowly moving recorder chart. Each of these surges appeared to occur at the same time that the collector electrodes in the outlet field of the precipitator were rapped. Thus, one of the conclusions based on the bolometer recordings is that the injection of ammonia was more effective in aiding fly-ash removal in the inlet and middle fields of the precipitator than in the outlet field, primarily because of the rapping losses that occurred in this field.

Fly-Ash Resistivity and Other Properties—

The results of determinations of the resistivity of fly ash at the inlets of Collectors 7A and 7B are given in Table 35. All of these data were obtained by the use of the point-plane probe and by the application of an electric field near the breakdown value in each collected sample. There is no indication that the injection of ammonia at any concentration (up to 14 ppm) caused a change in resistivity that was larger than the uncertainty in each measurement.

The results of analytical experiments with samples of the fly ash in aqueous slurries are given in Table 36. The pH data indicate that each sample produced a mildly acidic slurry but that the samples collected during ammonia injection were less acidic than those collected without injection. The ammonia concentrations appear to confirm the postulate that ammonia was present either in the form of a discrete particulate (such as ammonium sulfate) or a surface deposit on the fly ash. The sulfate concentrations apparently varied randomly as changes were made in ammonia injection.

Table 35. ELECTRICAL RESISTIVITY OF FLY ASH FROM A LOW-SULFUR COAL AT WIDOWS CREEK UNIT 7 (JUNE-JULY 1972)

Precipitator	Gas temp, °C	Injected NH_3 concn, ppm	Range of resistivity values, ohm cm
7A	138	0	$(1.6-2.7) \times 10^{11}$
		14	$(1.3-8.0) \times 10^{11}$
7B	132	0	$(3.6-3.7) \times 10^{11}$
		10	$(3.6-4.6) \times 10^{11}$
7B	143	0	$(2.2-3.9) \times 10^{11}$
		13	$(1.7-2.6) \times 10^{11}$
7B	149	0	$(2.8-5.9) \times 10^{11}$
		9	$(2.4-3.2) \times 10^{11}$

Table 36. CHEMICAL PROPERTIES OF FLY ASH FROM A LOW-SULFUR COAL AT WIDOWS CREEK UNIT 7 (JULY 1972)

Gas temp,[a] °C	Injected NH_3 concn, ppm	Sampling location	Ash properties		
			pH	Ammonia, wt %	Sulfate, wt %
132	0	Inlet	5.1	0.004	0.27
		Outlet	4.4	-	0.28
	10	Inlet	5.4	0.040	0.27
		Outlet	4.6	-	0.44
143	0	Inlet	4.9	0.005	0.35
	13	Inlet	6.0	0.061	0.27
149	0	Inlet	5.0	0.007	0.16
		Outlet	4.6	0.008	0.41
	9	Inlet	5.3	0.035	0.25
		Outlet	4.9	0.047	0.44

[a] Precipitator 7B.

Flue-Gas Concentrations--

Concentrations of ammonia, sulfur oxides, and water vapor found at the inlets to Collectors 7A and 7B are listed in Table 37. The data for ammonia and sulfur trioxide are of primary interest, as discussed below.

Table 37. CONCENTRATIONS OF FLUE GASES FROM A LOW-SULFUR COAL AT WIDOWS CREEK UNIT 7 (JUNE-JULY 1972)

Precipitator	Gas temp, °C	Injected NH_3 concn, ppm	Concentrations			
			NH_3, ppm	SO_3, ppm	SO_2, ppm	H_2O, %
7A	138	0	0.0	2.9	617	-
			0.0	1.7	621	-
		14	1.0	0.2	556	8.1
			0.4	0.3	626	8.3
			0.0	-	-	-
7B	132	0	0.6	4.0	565	-
			-	5.0	560	-
		10	0.9	0.8	554	8.4
			0.7	0.9	549	-
			-	0.6	528	-
7B	143	0	1.4	7.2	676	-
			0.6	5.0	670	-
			0.4	5.9	543	8.9
		13	0.9	1.5	638	8.7
			0.5	1.3	679	-
			0.6	-	-	-
7B	149	0	0.5	5.1	578	9.5
			0.5	4.2	577	-
		9	0.4	1.5	578	-
			-	0.9	599	-

Small concentrations of ammonia (less than 1 ppm) and somewhat larger concentrations of sulfur trioxide (3 to 6 ppm) were usually found without ammonia injection. The small concentrations of ammonia are attributed to slow bleeding of the conditioning agent into the flue gas even when the valves in the injection system were closed. The source of the ammonia may have been residual gas in the injection lines between the valves and the nozzles, or it may have been the cakes of ammonia-containing fly ash encrusted around the injection nozzles (these aggregates sometimes become very large and are known as "hornet nests"). The concentrations of sulfur trioxide found in the absence of deliberately injected ammonia are in a range of surprisingly high values when they are compared with the concentrations found in the flue gas from low-sulfur Western coals (Section V). Undoubtedly, the lower basicity of the ash at the Widows Creek plant was responsible for the comparatively high background concentrations of sulfur trioxide.

In each instance, the injection of ammonia lowered the concentration of sulfur trioxide. This observation is consistent with the occurrence of increased adsorption of sulfur trioxide on the surface of the fly ash as the acid on the surface is neutralized by ammonia. It is also consistent with the reaction of ammonia and sulfur trioxide (actually present as sulfuric acid) to produce particles of ammonium sulfate or ammonium bisulfate, as shown by the chemical equations on page 17.

Precipitator Electrical Data—

The configuration of the electrical sections of Collector A and the designations of the transformer-reactifier sets that power each section are shown schematically in Figure 8. The configuration of Collector B is identical to that of Collector A. The power supplies for Collector B are designated in essentially the same manner as those for Collector A; the only exception is the use of the term B in place of A.

During the brief study of Collector A, one member of the TVA technical staff investigated the waveforms of secondary voltage and secondary current produced by TR Set 7A2 in one of the two inlet sections of that precipitator. Peak values of each electrical parameter between sparks were first determined while ammonia was being injected at a concentration of 14 ppm; the results were: maximum voltage, 60 kV; maximum current, 1.00 A. The peak values of each parameter were again determined within a few minutes after ammonia injection had been discontinued; in this instance, the results were: maximum voltage, 58 kV; maximum current, 1.25 A. The results of the two determinations indicate that discontinuing ammonia injection rapidly brought about a decrease in the peak voltage and an increase in the peak current. Both effects were consistent with other observations of the electrical behavior of Collectors A and B with and without ammonia injection, as described subsequently.

During the study of Collector A, another type of experiment yielded the relationships between the time-average secondary current and voltage produced by TR Set 7A2 under manual

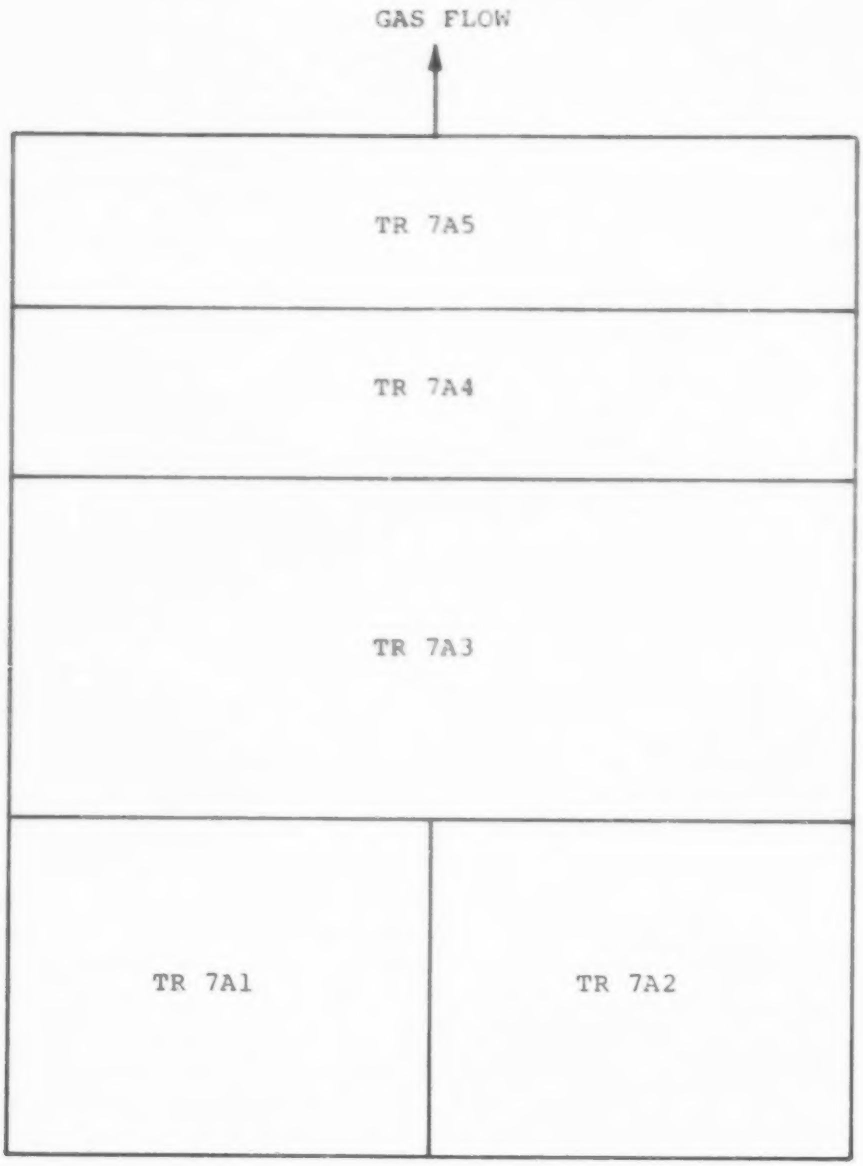
GAS FLOW
TR 7A5
TR 7A4
TR 7A3
TR 7A1
TR 7A2

Figure 8. Schematic diagram of electrical sections of Collector 7A at the Widows Creek plant

control. The results of this experiment are presented in Figure 9, with the observed values of current converted to the corresponding values of current density. Here, with dust-coated electrodes, the effect of ammonia injection was comparable to the effect on peak current and voltage that was observed with the set under automatic control—namely, a suppression of current density at a given voltage or an enhancement of voltage at a given current density.

During the subsequent study of Collector B, the information obtained with and without ammonia injection included the following: wave-form data for secondary voltages and currents of TR Sets 7B1 and 7B5 (powering electrical sections adjacent to the inlet and the outlet), time-average values of primary voltages and currents in all five sets, and time-average values of secondary voltages and currents of Sets 7B1 and 7B5 with clean electrodes. The data for these parameters are given in Tables 38 and 39 and in Figure 10. Here, the experimental data again indicate that ammonia injection tended to suppress current and enhance voltage with the effect being more pronounced in the inlet section of the precipitator.

Either of two interpretations may be given for the electrical data. One interpretation is that the electrical resistivity of fly ash on the collecting electrodes was higher with the injection of ammonia than without injection. This interpretation, however, cannot be reconciled with either the rapid change in the voltage and current waveforms or the shift in the location of the current-voltage curve for clean electrodes when injection was discontinued. The second interpretation, which would be consistent with all of the data, is that the electrical behavior of the gas stream rather than the deposited fly ash was altered by changes in the injection of ammonia. More explicitly, the second interpretation is that a fine particulate produced by the reaction of ammonia with the sulfur trioxide and water vapor normally present was electrically charged in the precipitator. Transfer of charge from molecular ions to small particles would lower the effective electrical conductivity of the gas stream, lowering the current produced by a given voltage. Alternatively, charging the small particles and simultaneously maintaining the original current would enhance the electric field in the gas stream through a space-charge effect.

Bull Run Plant, Collector C

The discussion of the initial trials of sulfur trioxide as a conditioning agent at the Bull Run plant in Section V of this report pointed out that trials of ammonia as a conditioning agent were also made. Whereas sulfur trioxide was initially injected into the flue gas entering Collector 1B, ammonia was

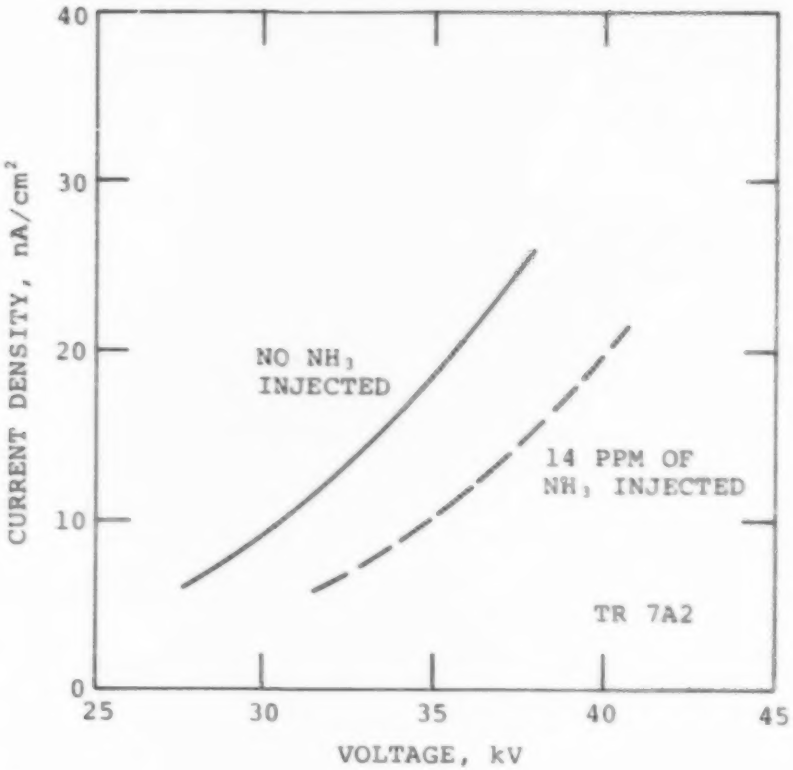

Figure 9. Current density *versus* voltage in Collector 7A of the Widows Creek plant (low-sulfur coal, June 1972)

Table 38. PEAK VALUES OF PRECIPITATOR SECONDARY VOLTAGES AND SECONDARY CURRENTS AT WIDOWS CREEK UNIT 7 (LOW-SULFUR COAL, JULY 1972)

Gas temp, °C	Injected NH_3 concn, ppm	TR Set 7B1 Voltage, V	TR Set 7B1 Current, A	TR Set 7B5 Voltage, V	TR Set 7B5 Current, A
132	0	54	1.10	62	2.00
	10	58	0.90	60	1.88
143	0	55	1.15	60	2.00
	13	57	0.80	59	2.00
149	0	55	1.15	57	1.63
	9	56	0.95	58	2.00

Table 39. PRIMARY VOLTAGES AND CURRENTS SUPPLIED BY THE TRANSFORMER-RECTIFIER SETS AT WIDOWS CREEK UNIT 7 (LOW-SULFUR COAL, JULY 1972)

TR Set	Injected NH_3 concn,[a] ppm	Voltage, V	Current, A
7B1	0	260	70
	13	280	56
7B2	0	230	67
	13	270	60
7B3	0	230	110
	13	245	105
7B4	0	300	75
	13	295	60
7B5	0	270	110
	13	270	110

[a] Temperature, 143°C.

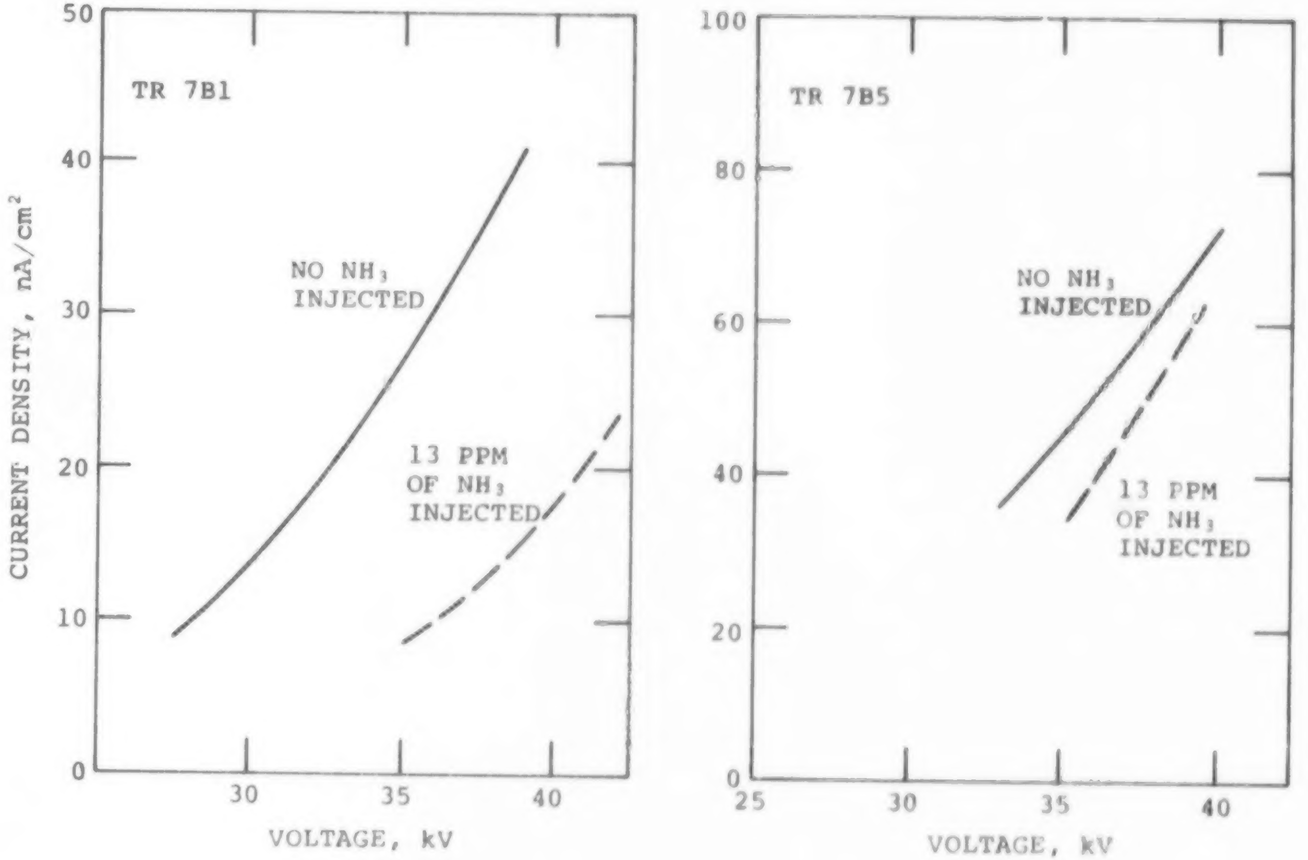

Figure 10. Current density *versus* voltage in Collector 7B of the Widows Creek plant (low-sulfur coal, July 1972)

injected into the gas entering Collector 1C. The two precipitators are identical, having the sectionalization previously shown in Figure 4. The transformer-rectifier sets energizing the electrical sections of Collector C are denoted by the same terms as those in Collector B except for the use of the letter C in place of B.

In the investigation of ammonia conditioning at Collector 1C of the Bull Run plant, all of the experimental approaches that have been discussed in connection with the Widows Creek plant were used. A lesser effort was put forth in completing some types of experimental work, however, in order to devote attention to a new procedure that was expected to confirm that ammonia conditioning occurred through a space-charge mechanism. This procedure involved the use of a condensation-nuclei counter in conjunction with diffusion batteries for detecting ultrafine particulate and classifying this material by size.[36]

Coal and Fly-Ash Compositions—

The experimental study of ammonia conditioning at the Bull Run plant was conducted on two occasions, first in September of 1972 and then in October of the same year. The experiments during September were terminated sooner than expected (because of a leaking boiler tube) before any sample of the coal had been collected. During the initial experiments in September, it was known that reclaim coal was used as the fuel; during the later experiments the same month, Haddix coal was burned. All of the experiments in October were conducted with Haddix coal as the fuel.

Previous analyses showed that the reclaim coal had a sulfur concentration varying between 0.9 and 1.6% and an ash concentration varying between 14.5 and 15.3% (page 45). During October, analyses of the Haddix coal yielded the following data:

Sulfur, 1.2%
Ash, 17.0%
Moisture, 5.7%
Heat value, 6,170 cal/g
(11,100 Btu/lb)

Compositions of fly ash produced from reclaim coal and Haddix coal are given in Table 40. The composition of the ash from reclaim coal is a repetition of the composition originally presented in Table 20. The composition of the ash from Haddix coal was determined by analyzing samples of ash from the hoppers of Collector 1C during the experiments in October. The two compositions are virtually identical.

Table 40. COMPOSITIONS OF FLY ASH
FROM THE BULL RUN PLANT
(Ammonia Conditioning, September-October 1972)

Component	Weight percentage	
	Reclaim coal	Haddix coal
Li_2O	0.04	0.04
Na_2O	0.23	0.27
K_2O	2.6	2.4
MgO	0.82	0.69
CaO	0.77	0.88
Al_2O_3	30.7	29.6
Fe_2O_3	6.8	5.7
SiO_2	53.2	54.9
TiO_2	1.9	2.2
P_2O_5	0.20	0.25

Precipitator Efficiencies—

Apparently, no comparison was made of the efficiencies of Collector 1C with and without ammonia injection. A comparison had been planned for the investigation during September, but it had to be cancelled because of the unscheduled plant outage. If a comparison was made later, the results are not available for inclusion in this report.

During the work in both September and October, efforts were made to obtain indirect indications of the effect of ammonia injection on the precipitator performance by use of a Bailey bolometer and recorder. The performance of the bolometer was not altogether satisfactory because imperfect maintenance permitted fly ash to accumulate on the lenses and thus to obscure changes occurring in ash concentrations in the precipitator effluent. Even so, the recorder usually indicated that starting ammonia injection decreased the opacity of the effluent and discontinuing injection increased the opacity, with response times being fairly brief after either change.

Fly-Ash Resistivity and Other Properties—

Fly-ash resistivity data were obtained with the point-plane probe and with the collected samples under approximately the electric field required for breakdown. All of these data were obtained during the initial experiments in September while Haddix coal was used as the fuel. The data are listed in Table 41. They indicate that the resistivity of the unconditioned ash was comparable to that of unconditioned ash from

Table 41. ELECTRICAL RESISTIVITY OF FLY ASH
AT THE BULL RUN PLANT
(AMMONIA CONDITIONING, SEPTEMBER 1972)

Injected NH_3 concn, ppm	Resistivity,[a] ohm cm
0	3.1×10^{10} 2.2×10^{10}
7	3.8×10^{10}

[a] Temperature, about 127°C.

reclaim coal (Table 21), which is not surprising because of the similarity in compositions of ash from the two coals. The data also indicate that 7 ppm of injected ammonia failed to produce a detectable change in the resistivity.

Analytical experiments with fly-ash samples in aqueous slurries yielded the data given in Table 42 for pH, soluble ammonia, and soluble sulfate. As indicated in the second column of this table, the ash samples were collected by three different methods: (1) insertion of an alundum thimble of the type employed for grain-loading measurements in the inlet duct of the precipitator; (2) insertion of a sampling train consisting of a cyclone, a cascade impactor, and a filter in series in the inlet and the outlet ducts; and (3) removal of material deposited in the precipitator hoppers. All of the pH values were in the acidic range; none of these data shows any effect of ammonia on the acidity of the ash. The concentrations of ammonia in the ash show increases as ammonia was injected (thimble samples), as the sampling location was moved toward the outlet of the precipitator (all types of samples), and as the particle size of the ash decreased (cyclone, impactor, and filter samples). The variation in the observed ammonia concentrations with each of the variations in sampling conditions is consistent with the assumed reaction of ammonia with naturally occurring sulfur trioxide and water vapor to produce a fine particulate of either ammonium sulfate or ammonium bisulfate.

Before the samples collected on filters were treated with water, they were examined by x-ray diffraction to determine whether either ammonium salt could be identified. The sample collected during ammonia injection at a concentration of 15 ppm produced weak diffraction bands in the locations expected for ammonium sulfate, but the diffraction pattern was not strong enough to be clearly identified.

Table 42. CHEMICAL PROPERTIES OF FLY ASH AT THE BULL RUN PLANT (AMMONIA CONDITIONING, OCTOBER 1972)

Injected NH_3 concn, ppm	Sample collector	Sampling location[a]	Ash properties		
			pH	Ammonia, wt %	Sulfate, wt %
0	Thimble	Inlet	4.5	<0.001	0.37
		Outlet	4.4	0.001	0.67
5	Thimble	Inlet	4.5	0.048	0.40
		Outlet	4.6	0.101	0.73
5	Cyclone	Inlet	-	0.04	-
	Impactor	Inlet	-	0.15	-
	Filter	Inlet	-	0.30	-
15	Cyclone	Outlet	-	0.15	-
	Impactor	Outlet	-	0.32	-
	Filter	Outlet	-	7.20	-
15	Hoppers	Inlet	4.8	0.033	0.20
		Outlet	4.6	0.048	0.37

[a] The terms "inlet" and "outlet" for samples other than the hopper samples refer to ducts entering and leaving the precipitator, respectively. These terms for hopper samples refer to locations of the hoppers under the electrical sections of the precipitator. Gas temperature, about 127°C.

Flue-Gas Concentrations—

Concentrations of flue gases at the precipitator inlet with and without ammonia injection are given in Table 43. These analytical data show the same effect of ammonia injection as the gas concentrations previously recorded for the Widows Creek plant (page 75): a decrease in the concentration of sulfur trioxide as a result of ammonia injection.

Precipitator Electrical Data—

Values of primary voltages, primary currents, secondary currents, and spark rates in the eight transformer-rectifier sets supplying power to Collector 1C under automatic control are given in Table 44. The data were recorded during one day of experimentation: first with no ammonia injected, then with 7 ppm of ammonia injected, and finally with ammonia injection

Table 43. CONCENTRATIONS OF FLUE GASES AT THE BULL RUN PLANT (AMMONIA CONDITIONING, SEPTEMBER 1972)

Injected NH_3 concn, ppm	Concentrations[a]			
	NH_3, ppm	SO_3, ppm	SO_2, ppm	H_2O, %
0	<0.3	1.3	640	-
	<0.3	1.8	680	-
	-	2.3	725	11.1
7	<0.3	0.8	711	-

[a] Temperature, about 127°C.

discontinued. These data show that after ammonia injection was started both primary and secondary currents decreased and that spark rates increased. Further, they show evidence of these changes being reversed after ammonia injection was discontinued.

Relationships between secondary voltages and secondary currents (computed as current densities) for the two power supplies at the precipitator inlet are shown in Figures 11 and 12. The data points shown as open symbols were recorded with the power supplies under manual control; the data points shown as closed symbols, on the other hand, were recorded with automatic control. Figure 11 shows the data recorded without any modification in the control circuitry. It shows that ammonia displaced the voltage-current curves to the right along the voltage axis, as expected from a space-charge effect, but it also shows curves with negative slopes that resulted from the heavy sparking induced by ammonia injection. Figure 12 shows the data recorded with a modification in the control circuitry that allowed data to be recorded at lower voltages where sparking did not occur even during ammonia injection. This figure shows simply a displacement in the voltage-current curve along the voltage axis, similar to the displacements found at the Widows Creek plant (pages 79 and 81).

Ultrafine Particle Concentrations—

As mentioned in the preliminary discussion of ammonia conditioning at the Bull Run plant, a condensation-nuclei counter equipped with diffusion batteries was used to detect the ultrafine particulate that was produced during ammonia injection.[36] The counter operates through the following procedure: a gas stream containing suspended particles is diluted with air, saturated with water vapor, cooled adiabatically to

Table 44. PRECIPITATOR ELECTRICAL DATA FROM THE BULL RUN PLANT
(AMMONIA CONDITIONING, SEPTEMBER 1972)

TR Set	NH_3 injection[a]	Time, min[b]	Primary voltage, V	Primary current, A	Secondary current, mA	Sparks per min
1LC[c]	Off	-	320	58	290	125
	On	5	290	50	260	300+
		10	305	45	230	300+
		60	300	34	200	300+
	Off	5	300	48	250	300+
		35	320	52	260	300+
2LC	Off	-	355	98	680	50
	On	5	370	94	600	300+
		10	370	88	560	300+
		60	380	68	500	300+
	Off	5	370	84	500	300+
		35	390	90	560	275
3LC	Off	-	370	76	380	175
	On	5	360	58	360	300+
		10	350	54	340	300+
		60	360	52	350	300+
	Off	5	360	52	360	300+
		35	380	63	360	300+
4LC	Off	-	370	62	350	55
	On	5	370	52	310	160
		10	370	50	290	300+
		60	360	48	300	300+
	Off	5	350	48	300	300+
		35	370	56	320	275

[a] Concentration in gas duct during injection, approximately 7 ppm.

[b] Readings were made before NH_3 injection was started, 5 to 60 min after it was started, and 5 to 35 min after it was stopped.

[c] One of two bushings was grounded, and thus the current was only about one-half of the normal value.

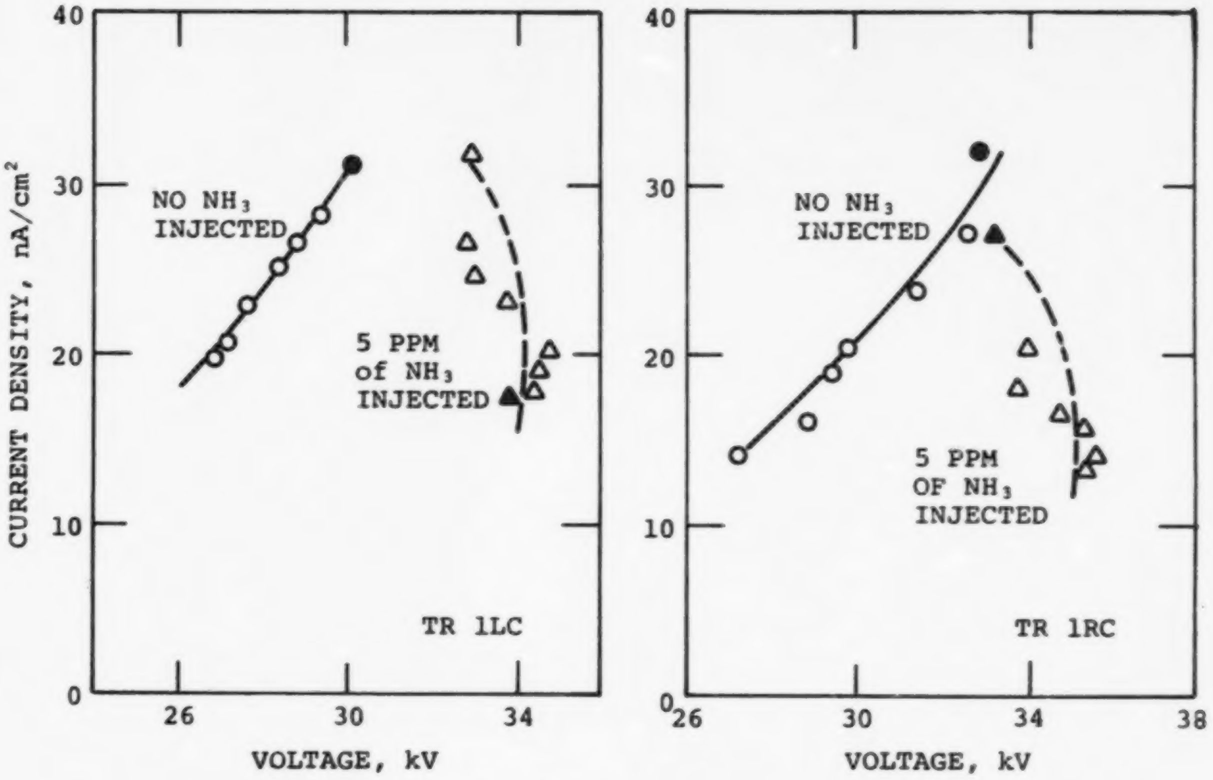

Figure 11. Current density versus voltage in Collector 1C of the Bull Run plant (ammonia conditioning, September 1972)

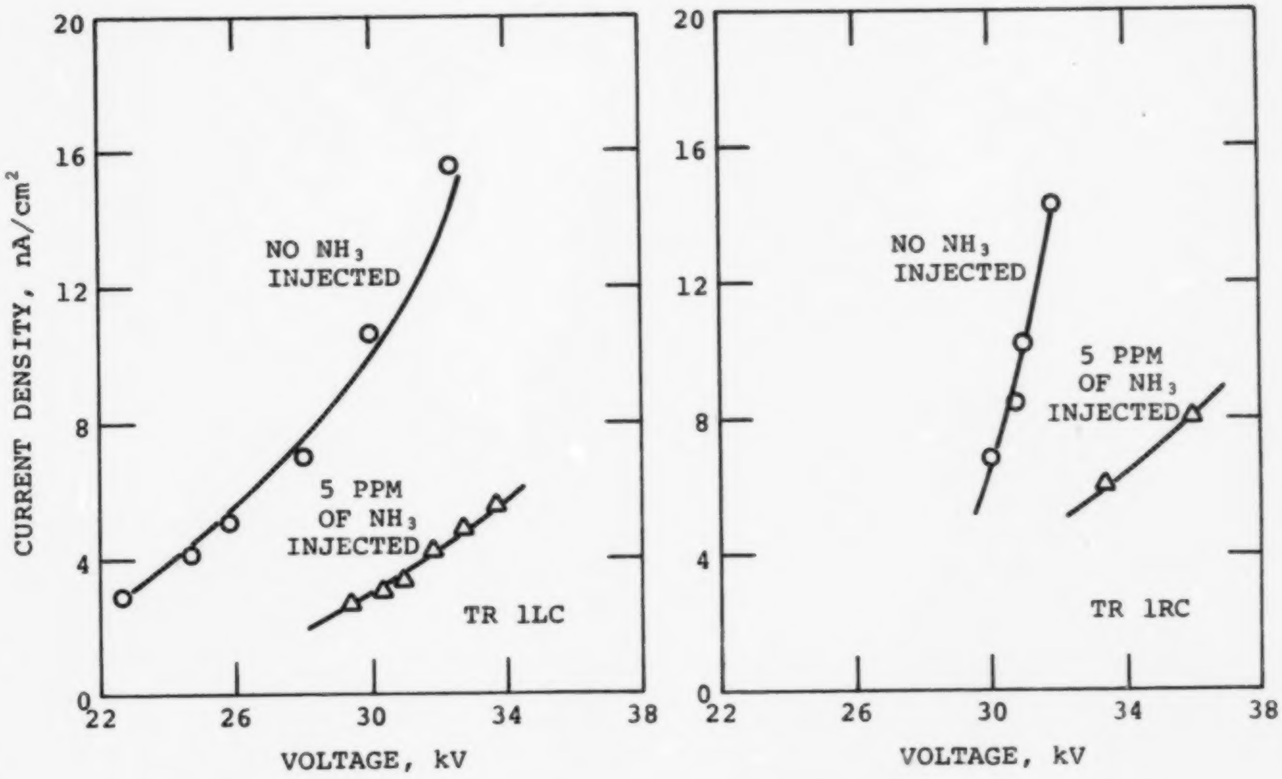

Figure 12. Current density *versus* voltage in Collector 1C of the *Bull Run* plant (ammonia conditioning, October 1972)

induce condensation of water vapor and growth of the particles, and then passed through a photoelectric counter that is able to detect the enlarged particles. The diffusion batteries permit particle-size classification; when one of the diffusion batteries is placed in the sampling line of the condensation-nuclei counter, it removes particles smaller than a characteristic size.

When the condensation-nuclei counter was used at the Bull Run plant, its sampling line included a cyclone and several stages of a Brink impactor to remove particles larger than 1.0 μm. Thus, the range of sizes of particles detected had an upper limit of 1.0 μm and a lower limit governed by the diffusion battery selected. The lower limit was estimated as about 0.005 μm when no diffusion battery was used; this is the size before growth in the presence of water vapor above the saturation level.

The results obtained with the condensation-nuclei counter and diffusion batteries are presented in Table 45. An important matter to be noted in examining the data in this table is that the data in each group were recorded during a brief time interval, usually 15 min or less. Emphasis should therefore be placed on the relative values of particle concentrations within each group as only one experimental parameter was altered (usually the ammonia concentration). Comparison of concentrations in different groups of data may be misleading because of varying sampling efficiencies and variations in the background concentrations of small fly-ash particles.

One observation to be made from the data in Table 45 is that changes in the rate of ammonia injection usually made significant changes in the concentration of particles counted. Although not shown by the table, these changes were observed very rapidly—in a matter of seconds—as the rate of injection was altered. The smallest effects of adding ammonia were observed when the flue-gas temperature was abnormally low—only 91°C rather than 124 to 127°C—which would have caused condensation of most of the sulfur trioxide vapor expected at the higher temperatures and thus would have permitted a much smaller amount of particulate to form as ammonia was injected.

In the experiments at the precipitator inlet, the increase in particle concentration did not appear to vary substantially with variations in the ammonia concentration from about 5 to 10 ppm. This observation gives weight to the assumption that only the particulate formed between sulfur trioxide and ammonia was detected in addition to the fly-ash particulate. For a given concentration of sulfur trioxide reactant, twice this value for the concentration of ammonia injected could theoretically convert all of the sulfur trioxide to ammonium

Table 45. CONCENTRATIONS OF SUBMICRON PARTICLES AT THE BULL RUN PLANT (AMMONIA CONDITIONING, OCTOBER 1972)

Gas temp, °C	Sampling location	Injected NH_3 concn, ppm	Minimum particle size, μm	Particle concn, no./cm^3
127	Inlet	0	<0.010	4.1×10^6
		6	<0.010	13.7×10^6
91	Inlet	0	<0.010	1.3×10^6
		4	<0.010	1.9×10^6
		12	<0.010	2.2×10^6
124	Inlet	0	<0.010	1.8×10^6
		5	<0.010	5.9×10^6
		10	<0.010	5.8×10^6
		0	<0.010	1.5×10^6
124	Inlet	5	<0.010	10.0×10^6
		5	0.014	8.9×10^6
		5	0.050	3.1×10^6
124	Inlet	5	<0.010	9.5×10^6
		0	<0.010	3.2×10^6
124	Outlet	0	<0.010	0.9×10^6
		Max.[c]	<0.010	7.6×10^6
		0	<0.010	1.0×10^6
124	Outlet	0	<0.010	1.0×10^6
		5	<0.010	3.1×10^6
		10	<0.010	3.4×10^6
		20	<0.010	6.9×10^6
		15	<0.010	5.9×10^6
		0	<0.010	1.1×10^6

[a] If other than <0.010 μm, controlled with a diffusion battery.

[b] Abnormally low during the gradual increase in unit load after an outage.

[c] Maximum attainable with the injection system but not determined, owing to the fact that the NH_3 flowmeter was inadvertently bypassed.

sulfate, and any greater concentration of ammonia injected could be unable to react with sulfur trioxide. Based on the sulfur trioxide concentrations given previously in Table 43, an ammonia concentration of about 5 ppm would have caused complete conversion of sulfur trioxide to ammonium sulfate particulate.

In comparatively limited work at the precipitator outlet, ammonia concentrations in the 15- to 20-ppm range appeared to produce more particulate than concentrations in the 5- to 10-ppm range. This finding may indicate that the concentration of ammonium sulfate particulate was governed not only by stoichiometric factors but by reaction kinetics and that the concentration was increased by the increased reaction time during gas flow through the precipitator.

A second observation to be made from the data in Table 45, based on a comparison of particle concentrations detected with and without diffusion batteries in the sampling line, is that at the precipitator inlet more than 50% of the particulate formed by ammonia injection was in the size range below 0.05 μm. Time did not allow any study of particle size at the precipitator outlet. It is possible, however, that the size range was even smaller at the outlet than at the inlet. This possibility is suggested by the fact that the experimental data give no indication of a reduction in number concentration across the precipitator, despite other evidence cited later indicating that a reduction in mass concentration did occur at other power plants.

POWER PLANTS BURNING HIGH-SULFUR COALS

Widows Creek Plant, Unit 7

During November of 1972, a study was made of ammonia conditioning at Unit 7, Collector 7A, of the Widows Creek plant while the customary high-sulfur coal was being burned as the fuel. Analyses of coal samples over a period of several days indicated that the following properties of the coal were representative of the properties prevailing during the investigation:

Sulfur, 3.5%
Ash, 13.8%
Moisture, 6.5%
Heat value, 6,330 cal/g (11,400 Btu/lb)

Analysis of the fly ash gave the composition shown by Table 46. This composition differs from the compositions of fly ash from other Eastern coals in having a higher percentage of calcium oxide, but the percentage of calcium oxide is still lower than the values for ash from the Western coals discussed in Section V.

Table 46. COMPOSITION OF FLY ASH FROM A HIGH-SULFUR COAL AT WIDOWS CREEK UNIT 7 (November 1972)

Component	Weight percentage
Li_2O	0.02
Na_2O	0.49
K_2O	2.6
MgO	0.94
CaO	3.7
Al_2O_3	19.0
Fe_2O_3	22.0
SiO_2	48.1
TiO_2	1.0
P_2O_5	0.26
SO_3	1.0

No determination of the precipitator efficiency was made during the study at the Widows Creek plant in November, 1972. However, the results from earlier efficiency tests by TVA[35] at Collector B of Unit 7 (identical to Collector A) are given in Table 47. These results were obtained while high-sulfur coal was being burned as a fuel, and the data obtained with ammonia conditioning presumably indicate the effects on efficiency that were produced by ammonia conditioning during the investigation discussed in this report.

During this investigation, an effort was made to use a Bailey bolometer to obtain indirect indications of the effects on precipitator efficiency that were produced by ammonia conditioning. In several experiments, the bolometer did not function satisfactorily because of insufficient efforts to keep lenses free of dust accumulations. When the performance of the instrument was relatively satisfactory, the bolometer indicated that the injection of ammonia caused a gradual suppression in both the time-average particulate concentration in the precipitator effluent and the intensity of rapping puffs emitted by the precipitator during rapping. On the

Table 47. PRECIPITATOR EFFICIENCIES WITH HIGH-SULFUR COAL AT WIDOWS CREEK UNIT 7 (JUNE-JULY 1970)[a]

Gas temp, °C	Injected NH_3 concn, ppm	Gas velocity, relative value[b]	Efficiency, %
ca. 145	0	0.95	96
		1.00	94
		1.05	92
ca. 130	0	0.95	87
		1.00	84
		1.05	78
ca. 130	ca. 11	0.95	>99
		1.00	98[c]
		1.05	97[c]

[a] Assumed to indicate approximate efficiencies during the investigation.

[b] Relative to the design value of 2.42 m/sec.

[c] Estimated by extrapolation of data at lower gas velocities. Believed to be conservative estimates from the available data.

other hand, the instrument indicated that the discontinuance of ammonia injection caused a relatively rapid reversal of the initial effects.

Overall, the investigation of ammonia conditioning at the Widows Creek plant with high-sulfur coal as the fuel consisted of the same experimental approaches as the previous studies at this plant and the Bull Run plant with low-sulfur coals. The experimental data are given in detail in Tables 48 through 52 and Figure 13, and are presented on the following pages. The principal observations to be made from an inspection of the experimental data are as follows:

- Fly-ash resistivity (Table 48). No increase in the resistivity of the ash was detected as the result of ammonia injection at either of the two flue-gas temperatures investigated, 132 or 154°C, contrary to the prediction based on the earlier work of Reese and Greco.[5] A decrease in resistivity was apparent at the higher temperature. However, in view of the moderate resistivity of the unconditioned ash, this change (if real) could not have been responsible for an improvement in precipitator performance.

Table 48. ELECTRICAL RESISTIVITY OF FLY ASH FROM A HIGH-SULFUR COAL AT WIDOWS CREEK UNIT 7 (NOVEMBER 1972)

Gas temp, °C	Injected NH_3 concn, ppm	Resistivity, ohm cm
132	0	2.8×10^8
		1.0×10^8
		1.1×10^8
	20	1.0×10^8
		3.0×10^8
154	0	3.9×10^{10}
		1.3×10^{10}
	22	7.1×10^8
		4.2×10^8

Table 49. CHEMICAL PROPERTIES OF FLY ASH FROM A HIGH-SULFUR COAL AT WIDOWS CREEK UNIT 7 (NOVEMBER 1972)

Injected NH_3 concn, ppm	Sample collector	Sampling location[a]	Ash properties		
			pH	Ammonia, wt %	Sulfate, wt %
0	Thimble	Inlet	10.3	<0.001	1.49
		Outlet	10.6	0.009	1.39
20	Thimble	Inlet	10.0	0.117	1.57
		Outlet	10.0	0.127	2.15
0	Hoppers	Inlet	10.8	0.010	0.76
		Outlet	10.7	0.016	0.94
20	Hoppers	Inlet	10.7	0.044	0.92
		Outlet	10.3	0.074	1.42

[a] The terms "inlet" and "outlet" for samples other than the hopper samples refer to ducts entering and leaving the precipitator, respectively. These terms for hopper samples refer to locations of the hoppers under the electrical sections of the precipitator. Gas temperature, about 132°C.

Table 50. CONCENTRATIONS OF FLUE GASES FROM A HIGH-SULFUR COAL AT WIDOWS CREEK UNIT 7 (NOVEMBER 1972)

Gas temp, °C	Injected NH_3 concn, ppm	Concentrations			
		NH_3, ppm	SO_3, ppm	SO_2, ppm	H_2O, %
132	0	0.14	10.5	2410	7.8
		0.06	13.1	2500	6.8
		0.07	9.5	2620	8.0
	11	0.09	6.9	2400	8.3
		0.09	6.5	2430	-
		-	6.3	2580	-
	20	0.06	9.1	2420	8.2
		0.04	5.0	2370	-
		0.06	3.2	1820	-
154	0	-	8.7	1410	8.5
		-	9.8	1800	-
		-	12.3[a]	2450[a]	7.4[a]
		-	10.9[a]	2200[a]	-
	22	0.37[a]	2.9[a]	2510[a]	7.7[a]
		-	1.0[a]	2430[a]	-
		-	0.5[a]	2570[a]	-

[a] These concentrations were determined at the precipitator outlet. All others in this table were determined at the inlet.

Table 51. PRECIPITATOR ELECTRICAL DATA FROM WIDOWS CREEK UNIT 7 (HIGH-SULFUR COAL, NOVEMBER 1972)

TR Set	Injected NH_3 concn, ppm	Primary data[a] Voltage, V	Primary data[a] Current, A	Secondary data[a] Voltage, kV	Secondary data[a] Current, mA
7A1	0	295	70	-	-
	23	325	66	-	-
7A2	0	290	72	43.7	234
	23	300	67	47.3	248
7A3	0	275	200	-	-
	23	285	185	-	-
7A4	0	195	90	-	-
	23	210	110	-	-
7A5	0	275	180	40.5	685
	23	275	175	40.9	665

[a] Each of the electrical values listed with ammonia injection was essentially at steady-state within a few minutes after injection was started.

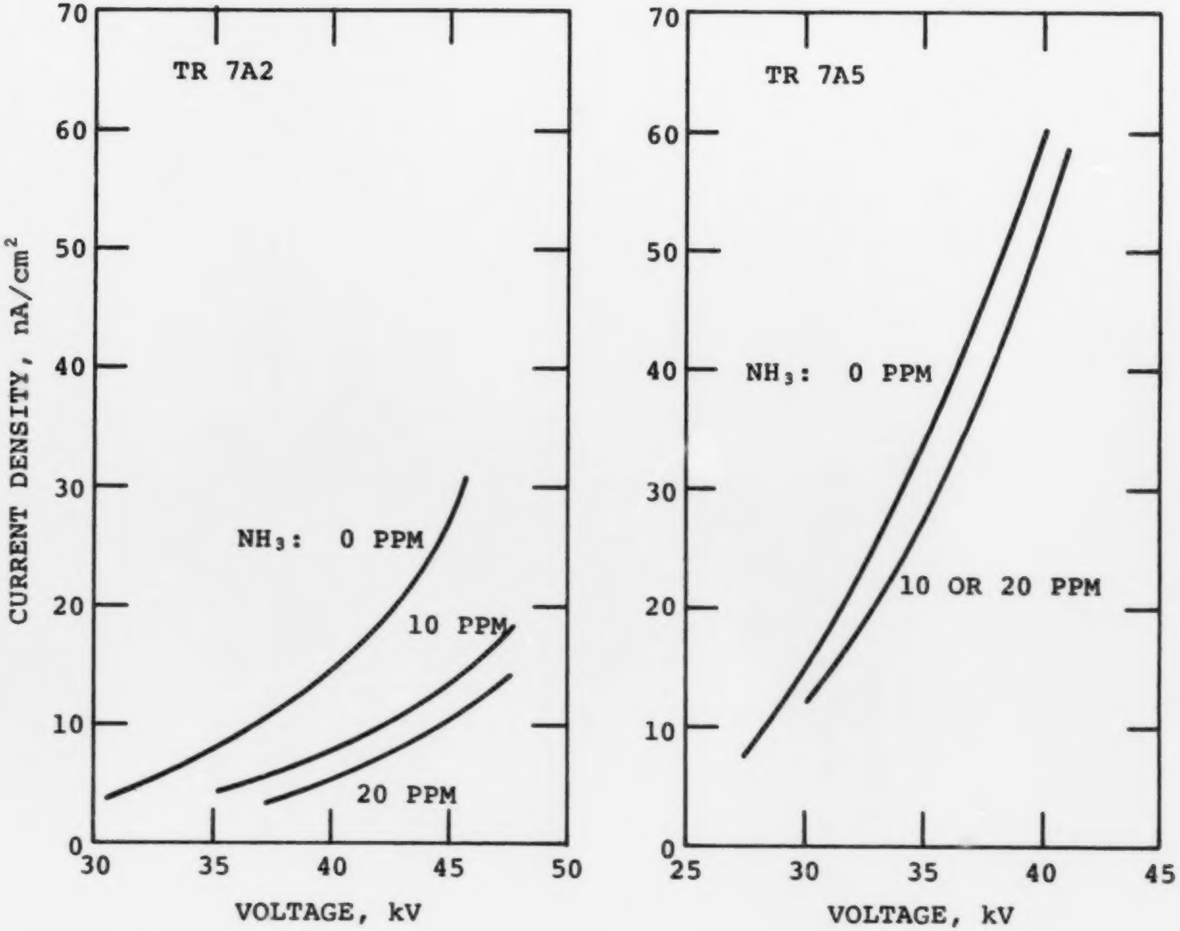

Figure 13. Current density versus voltage in Collector 7A of the Widows Creek plant (high-sulfur coal, November 1972)

Table 52. CONCENTRATIONS OF SUBMICRON PARTICLES AT THE WIDOWS CREEK PLANT (HIGH-SULFUR COAL, NOVEMBER 1972)

Sampling location[a]	Injected NH_3 concn, ppm	Minimum size detected, μm	Particle concn, no./cm	No. % above minimum size
Inlet	0	0.005	6.5×10^6	100
		0.014	5.4×10^6	83
		0.050	2.9×10^6	45
Inlet	11	0.005	19.5×10^6	100
		0.014	16.7×10^6	85
		0.050	11.2×10^6	57
Inlet	0	0.005	12.0×10^6	100
		0.014	10.3×10^6	89
		0.050	6.3×10^6	52
Inlet	23	0.005	30.9×10^6	100
		0.014	29.0×10^6	94
		0.050	17.0×10^6	55
Outlet	0	0.005	0.43×10^6	100
		0.014	0.35×10^6	81
Outlet	20	0.005	1.40×10^6	100
		0.014	0.98×10^6	70
		0.050	0.79×10^6	56

[a] Gas temperature, 132°C.

- Fly-ash properties in aqueous slurries (Table 49). Samples of fly ash were collected from the gas ducts entering and leaving the precipitator and from the hoppers of the precipitator. Analyses of the ash in aqueous slurries showed that the concentration of ammonia in the ash increased markedly when the conditioning agent was injected into the gas stream.

- Flue-gas concentrations (Table 50). The injection of ammonia always lowered the concentration of sulfur trioxide in the gas stream entering the precipitator.

- Precipitator electrical data (Table 51 and Figure 13). The injection of ammonia caused a rapid change in the electrical behavior of the precipitator, most notably a shift in the secondary voltage-current curve toward higher voltages for a given current density or toward a lower current density for a given voltage.

- Ultrafine particulate concentrations (Table 52). The condensation-nuclei particle counter showed rapid increases in fine-particle concentrations as ammonia injection was started and rapid reversal of this effect as injection was stopped. The effects were less pronounced at the outlet of the precipitator than at the inlet, suggesting that a large fraction of the small particulate introduced by ammonia injection was collected in the precipitator.

All of the above observations are consistent with the occurrence of ammonia conditioning through the space-charge effect, which has previously been hypothesized as the explanation for ammonia conditioning at the Widows Creek and Bull Run plants with low-sulfur coals.

Gallatin Plant, Unit 4

During the first part of 1973, TVA made a preliminary installation of ammonia conditioning facilities at the Gallatin plant. The initial installation permitted treatment of one-third of flue gas emitted from Unit 4 (290 MW), which passed through one of the three electrostatic precipitators for this unit (Collector 4C). The success achieved in treating flue gas from high-sulfur coal led to an enlargement of the ammonia conditioning system to treat all of the flue gas from each of the four units at the Gallatin plant. The enlargement of the system was completed early in 1974, at which time the Institute made a study of the conditioning process at Collector 4C.

Coal and Fly-Ash Properties—

The coal burned in Unit 4 of the Gallatin plant during the investigation of ammonia conditioning was high in sulfur content. Representative properties of the coal samples collected during this investigation are shown below:

Sulfur, 4.0%
Ash, 14.2%
Moisture, 7.0%
Heat value, 6,300 cal/g
(11,300 Btu/lb)

Samples of fly ash collected from the hoppers of Collector 4C varied significantly in the concentrations of several components, principally calcium oxide and sulfur trioxide. In the composition shown in Table 53, the ranges of concentrations of these two components are given with the average concentrations of the remaining components.

Table 53. COMPOSITION OF FLY ASH FROM GALLATIN UNIT 4

Component	Weight percentage
Li_2O	0.02
Na_2O	0.62
K_2O	2.6
MgO	0.97
CaO	1.2-2.9
Al_2O_3	21.6
Fe_2O_3	19.9
SiO_2	46.9
TiO_2	2.0
P_2O_5	0.29
SO_3	1.2-2.3

Precipitator Efficiencies—

There are no data available that would permit a comparison of the absolute efficiencies of Collector 4C with and without ammonia injection. The manifold for injecting ammonia was placed in the original sampling ports that were designed for grain-loading measurements upstream from the precipitator. Thus, since this manifold was installed, the only measurements relative to efficiency have consisted of measurements at the outlet of the precipitator.

The results of TVA's grain-loading measurements at the outlet of Collector 4C[37] are given in Table 54. These data were obtained during February of 1973 with the original conditioning facilities in operation. The data indicate that 18 ppm of ammonia lowered the emission level by about 75% at 143°C (the usual flue-gas temperature in the precipitator) and 32 ppm lowered the emission level by about 65% at 154°C.

Table 54. FLY-ASH EMISSION FROM GALLATIN UNIT 4 (COLLECTOR 4C)

Gas temp, °C	Injected NH_3 concn, ppm	Outlet dust concn, g/m^3 (gr/ft^3)
143	0	0.338 (0.147)
	18	0.081 (0.035)
154	0	0.299 (0.130)
	32	0.108 (0.047)

Use of an Anderson impactor during the investigation of February, 1974, yielded values of the total particulate concentration plus the particulate concentrations in various ranges of effective diameter between the limits of 0.38 µm and 10.8 µm. The data obtained with this impactor do not necessarily reflect the overall emission levels, in contrast with the data obtained by TVA, for the sampling nozzle of the impactor was always at the same location within the outlet duct, at an insertion of about 1 m into the duct at one of the six ports used by TVA with multiple insertions in all ports. Moreover, one series of experiments was conducted with the rappers in operation and another series was conducted with the rappers deenergized, whereas the tests by TVA were all performed with the electrode rappers in operation.

The results obtained with the Andersen impactor are presented in Table 55. Inspection of the total concentrations found with the rappers in operation indicates that the injection of 20 ppm of ammonia lowered the concentration from 0.227 to 0.142 g/m^3 (0.0987 to 0.0617 gr/ft^3). Comparison of the data obtained with the rappers not in operation indicates that 20 ppm of ammonia lowered the concentration from 0.135 to 0.016 g/m^3 (0.0589 to 0.0069 gr/ft^3). Further comparison of the data obtained with and without rapping, either with or without ammonia injection, indicates that reentrainment of particulate as the result of rapping contributed markedly to the level of particulate emission.

Table 55. EMISSION OF FLY ASH IN VARIOUS SIZE RANGES AT GALLATIN UNIT 4 (COLLECTOR 4C)[a]

Rappers	Particle size, µm	Outlet dust concentration, g/m³ (gr/ft³) No NH_3 injected	Outlet dust concentration, g/m³ (gr/ft³) 20 ppm of NH_3 injected
On	>10.8	0.1520 (0.0661)	0.0764 (0.0332)
	10.8-6.7	0.0136 (0.0059)	0.0248 (0.0108)
	6.7-4.5	0.0060 (0.0026)	0.0173 (0.0075)
	4.5-3.1	0.0025 (0.0011)	0.0099 (0.0043)
	3.1-2.0	0.0018 (0.0008)	0.0053 (0.0023)
	2.0-0.96	0.0039 (0.0017	0.0039 (0.0017)
	0.96-0.57	0.0133 (0.0058)	0.0012 (0.0005)
	0.57-0.38	0.0147 (0.0064)	0.0002 (0.0001)
	<0.38	0.0191 (0.0083)	0.0030 (0.0013)
	Total	0.2270 (0.0987)	0.1419 (0.0617)
Off	>10.8	0.1104 (0.0480)	0.0087 (0.0038)
	10.8-6.7	0.0069 (0.0030)	0.0009 (0.0004)
	6.7-4.5	0.0046 (0.0020)	0.0002 (0.0001)
	4.5-3.1	0.0030 (0.0013)	0.0002 (0.0001)
	3.1-2.0	0.0030 (0.0013)	0.0002 (0.0001)
	2.0-0.96	0.0030 (0.0013)	0.0007 (0.0003)
	0.96-0.57	0.0014 (0.0006)	0.0002 (0.0001)
	0.57-0.38	0.0002 (0.0001)	0.0002 (0.0001)
	<0.38	0.0030 (0.0013)	0.0044 (0.0019)
	Total	0.1355 (0.0589)	0.0159 (0.0069)

[a] Gas temperature, 138°C.

The injection of ammonia was evidently helpful in lowering the total emission of particulate with or without rapping. The effect of ammonia with rapping may be attributed to either or both of two mechanisms of conditioning: (1) an increase in the cohesiveness of fly-ash particles and (2) an increase in the space-charge component of the electric field. The effect of ammonia without rapping probably can be attributed to the space-charge effect alone.

The data in Table 55 for the concentrations of particulate in various particle-size ranges indicate that with rapping the injection of ammonia actually increased the concentrations in all diameter ranges between 2.0 and 10.8 µm while causing a decrease in the total concentration. The particle-size data obtained without rapping do not show this effect from the injection of ammonia. It seems reasonable to draw from these observations the conclusion that the injection of ammonia during rapping increased the size of agglomerates of fly ash that were reentrained, an effect that might well be expected as the result of conditioning through the mechanism of increased cohesiveness of individual particles.

Information about the concentration of fly ash emitted from the precipitator were also obtained with a Bailey bolometer, as discussed in detail later in this report (pages 110 through 113). The bolometer confirmed the findings with the Andersen impactor indicating that the injection of 20 ppm of ammonia markedly lowered the level of particulate emission from the precipitator with the rappers in service. Also, this instrument confirmed the conclusion from the impactor data indicating that, either with or without the injection of ammonia, the discontinuance of rapping sharply lowered the level of emission (it was unable, however, to show the difference in the levels of emission with and without ammonia injection that were found with the impactor while the rappers were not in service).

Fly-Ash Resistivity—

The results of determinations of the fly-ash resistivity with the point-plane resistivity probe are given in Table 56. There is an indication from some of the data that the injection of ammonia lowered the resistivity of the ash. However, the poor reproducibility of the data make it uncertain that the apparent effect was real. In any event, there is no indication of an increase in resistivity, the phenomenon originally suggested by earlier work on ammonia conditioning of fly ash from high-sulfur coal.

Voltage-current data presented later in this report indicate that the injection of ammonia either increased the resistivity of the ash on the collecting electrodes or altered the electrical properties of the gas stream through a space-charge effect. The rapidity of the changes in the electrical data and the stability of the adjusted values with time after injection was started or stopped strongly indicates that the effect was on the gas stream, not on the deposited ash.

Evidence of Conditioning through a Space-Charge Effect—

In the studies of ammonia conditioning of the Widows Creek and the Bull Run plants, the evidence for conditioning through a space-charge effect consisted of the following: (1) fly-ash analyses showing the presence of ammonia as a component of particulate material collected either from the inlet and outlet ducts or from the hoppers of the precipitator; (2) flue-gas analyses showing loss of sulfur trioxide from the gas phase when ammonia was injected; (3) rapid changes in the electrical behavior of the precipitator power supplies; and (4) rapid appearance and disappearance of ultrafine

Table 56. ELECTRICAL RESISTIVITY OF FLY ASH AT GALLATIN UNIT 4

Gas temp, °C	Injected NH_3 concn, ppm	Resistivity, ohm cm, at different electric fields: 2 kV/cm	Resistivity, ohm cm, at different electric fields: 10 kV/cm
138	0	14.0×10^8	2.9×10^8
		3.8×10^8	1.3×10^8
		92.0×10^8	14.0×10^8
		7.9×10^8	1.9×10^8
	10	0.9×10^8	0.3×10^8
		0.5×10^8	0.1×10^8
	20	8.2×10^8	4.2×10^8
		2.1×10^8	0.8×10^8
132	0	50.0×10^8	1.1×10^8
		10.0×10^8	2.9×10^8
	20	16.0×10^8	5.3×10^8

particulate detected with the condensation-nuclei counter when ammonia injection was started or stopped.

In the studies of ammonia conditioning at the Gallatin plant, each type of evidence for the space-charge effect was once again obtained. The experimental data indicating the occurrence of the space-charge effect are presented in Tables 57 through 60 and Figures 14 and 15 on the pages immediately following. The data are self-explanatory in nearly all instances, in view of their similarity to similar data that have been discussed previously in this report. Thus, no detailed commentary on the data seems necessary. However, attention is directed particularly to Figure 14, which shows very clearly how rapidly the electrical behavior of the precipitator responded to the injection of ammonia.

Evidence of Conditioning through an Apparent Change in the Cohesiveness of Fly-Ash Particles—

The possibility that ammonia conditioning involved a change in the cohesive forces between fly-ash particles as well as the space-charge effect was considered for several reasons. First, TVA personnel with experience in ammonia conditioning believe that an increase in cohesiveness occurs; they base this belief on observations of phenomena such as (1) the formation of large agglomerates of particulate known as "hornet nests" around the ammonia injection probes, (2) the

Table 57. CHEMICAL PROPERTIES OF FLY ASH AT GALLATIN UNIT 4[a]

Injected NH_3 concn, ppm	Ash properties		
	pH	Ammonia, wt %	Sulfate, wt %
0	8.6	<0.01	1.2
20	8.6	0.21	1.7

[a] Collected at the precipitator inlet in an alundum thimble at a gas temperature of 138°C.

Table 58. CONCENTRATIONS OF FLUE GASES AT GALLATIN UNIT 4

Gas temp, °C	Injected NH_3 concn, ppm	Concentrations			
		NH_3, ppm	SO_3, ppm	SO_2, ppm	H_2O, %
138	0	<0.1	6.9	2630	8.8
		<0.1	9.2	2980	8.2
	10	<0.1	0.9	2580	-
		<0.1	0.9	2760	-
	20	0.9	1.8	3310	-
		2.0	<0.9	3180	9.7
132	0	-	7.4	3390	8.9
		-	7.4	3450	-
	20	0.5	<0.9	3500	-
		3.5	<0.9	3480	-

Table 59. PRECIPITATOR ELECTRICAL DATA FROM GALLATIN UNIT 4

		Primary data		Secondary data		
TR Set[a]	Injected NH_3 concn, ppm	Voltage, V	Current, A	Voltage, kV	Current density, nA/cm	Sparks per min
4C1	0	378	70	38.0	42.3	0
	20	382	37	45.6	19.4	70
4C2	0	322	73	33.5	42.8	0
	20	363	72	39.9	42.3	26
4C3	0	313	77	30.7	46.3	0
	20	326	77	33.1	46.9	0
4C4	0	313	76	29.6	45.5	0
	20	320	76	30.1	45.8	0

[a] Listed in the sequence from the inlet to the outlet of the precipitator.

Table 60. CONCENTRATIONS OF SUBMICRON PARTICLES AT GALLATIN UNIT 4

		Particle concn, no./cm , as a function of minimum size		
Sampling location	Injected NH_3 concn, ppm	0.005 μm	0.014 μm	0.064 μm
Inlet	0	22×10^6	17×10^6	-
	>20[a]	61×10^6	26×10^6	-
Outlet	0	-	0.5×10^6	0.2×10^6
	20	-	1.5×10^6	0.9×10^6

[a] Uncertain as a result of a broken flowmeter in the injection system.

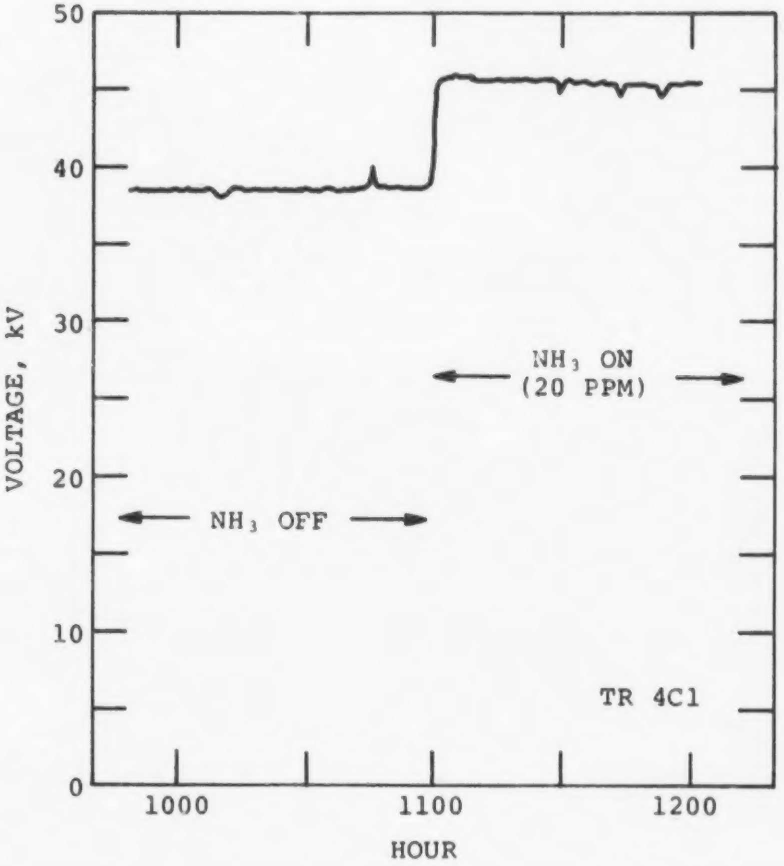

Figure 14. Rapidity of the effect of ammonia injection on the voltage supplied to the inlet electrical field of Gallatin Precipitator 4C

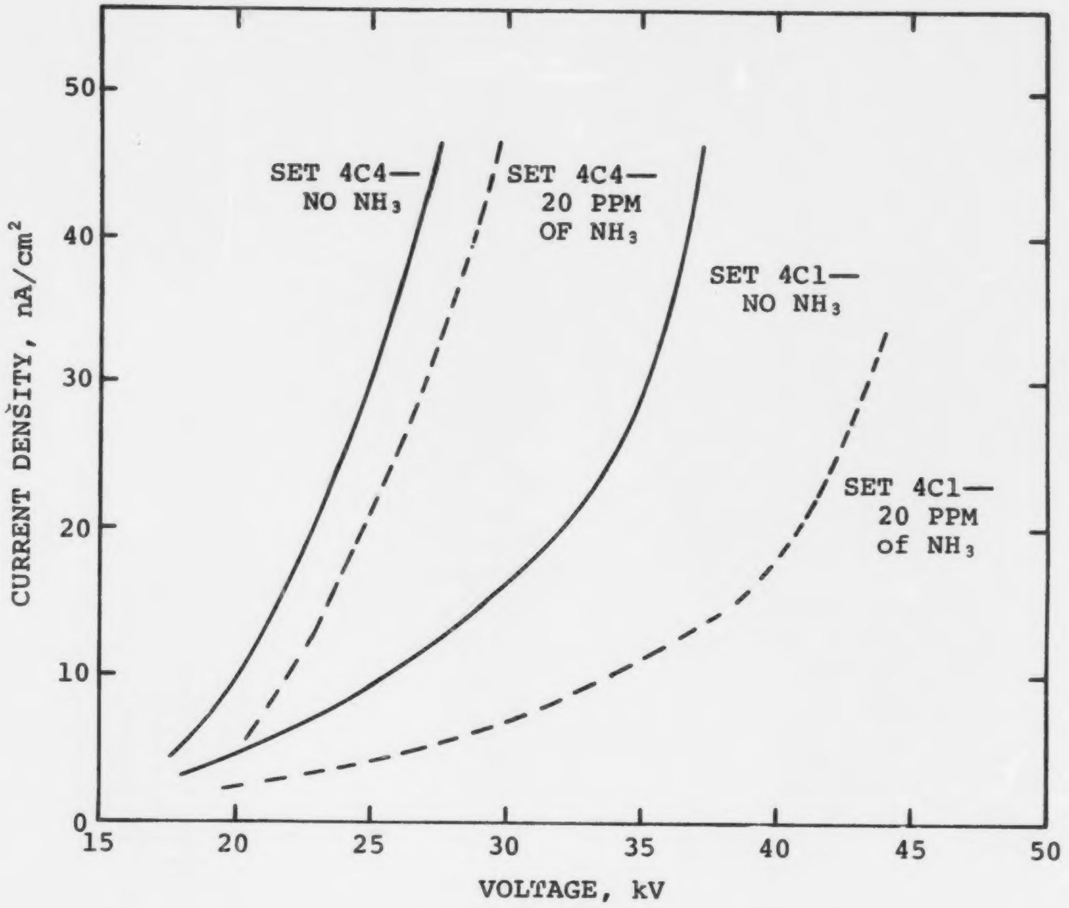

Figure 15. Current density *versus* voltage in Precipitator 4C of the Gallatin plant

accumulation of ash deposits on exhaust fans between precipitators and stacks, and (3) the apparent "stickiness" of ash in systems for removing ash from precipitator hoppers. Second, Institute personnel using a Brink impactor at the Bull Run plant noted a distinct difference in the compactness of ash deposited within the impactor when ash samples were collected with and without ammonia conditioning. Third, representatives of the Koppers Company who have had considerable experience with ammonia conditioning believe that ammonia increases the cohesiveness of fly ash; moreover, they have taken photomicrographs of ash particles that reportedly reveal the agglomeration of spheres of fly ash through bridges of a feather-like material thought to be ammonium sulfate.[38] Finally, Dalmon and Tidy[15] have reported that the use of ammonium sulfate as a conditioning agent may increase the efficiency of collection of fly ash, especially if the effective electrical resistivity of the ash is low as the result of the presence of a substantial amount of low-resistivity carbon particles. Increasing the cohesiveness of low-resistivity fly ash would, of course, provide a mechanical force to hold the ash on the collecting electrodes of a precipitator, taking the place of the electric force associated with high-resistivity ash and thus minimizing reentrainment.

The evidence for an increase in the cohesiveness of fly-ash particles consisted of the data obtained with two types of photoelectric measurements at the precipitator outlet. One type of measurement was made with a Bailey bolometer to detect changes in the obscuration of a light beam across the outlet duct. The other type of measurement was made with a light-scattering photometer known as a Climet Particle Analyzer (Model No. CT-201).[36] Both the Bailey bolometer and the Climet counter gave real-time indications of the rate of change in the level of particulate emission as a change in ammonia injection was made.

The results obtained with the Bailey bolometer during one day of experimentation are shown by a reproduction of the recorder chart in Figure 16. During the first period of about 4 hr before the injection of ammonia was started, the bolometer gave evidence of wide variations in the degree of light obscuration; the recorder chart showed numerous spikes of high intensity that were presumably caused by puffs of fly ash reentrained during electrode rapping. During the following period of about 4 hr with 20 ppm of ammonia injected, the spikes were continued at about the same magnitude for about 30 min but then were gradually suppressed during the remaining time of ammonia injection. After ammonia injection was discontinued, the spikes remained suppressed for

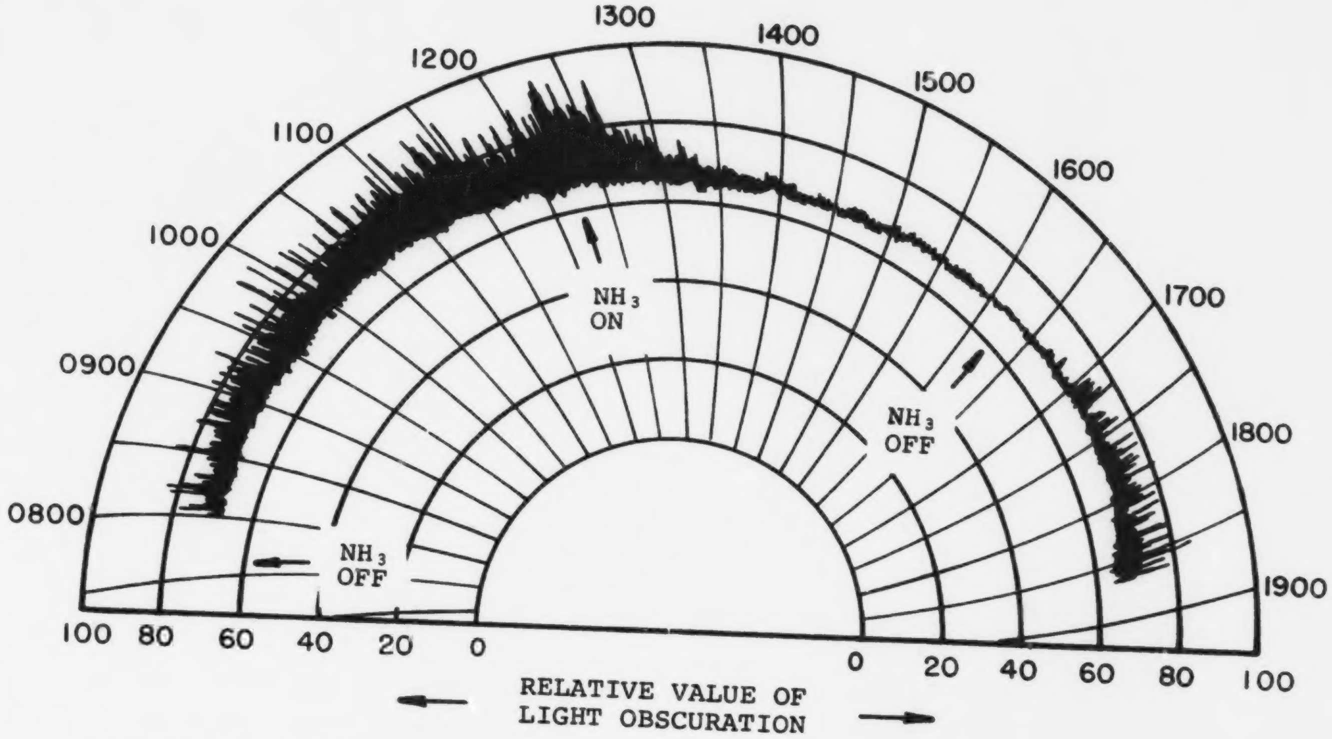

Figure 16. Effects of changes in ammonia injection on the emission of particulate from Gallatin Precipitator 4C as indicated by the Bailey bolometer (20 ppm of NH_3)

about 1 hr but then gradually increased in magnitude until they approached the original magnitude. It is evident that changes in the intensity of the rapping spikes occurred over extended times following each change in ammonia injection, in contrast to the changes in electrical data which were very rapid.

The results obtained with the bolometer during another day of experimentation as shown in Figure 17. This reproduction of the recorder chart shows the information obtained with and without electrode rapping, first with no ammonia injected and then with 20 ppm of ammonia injected. The deenergization of the rappers caused the disappearance of rapping spikes, with or without ammonia injection, and the recorder pen traced essentially a smooth curve that was indicative of minimal obscuration. The beginning of ammonia injection with the rappers energized caused a gradual rather than an immediate suppression of the rapping spikes similar to that described above.

The data obtained with the Climet particle counter are given in Table 61. These data consist of the concentrations by number of particles in two size ranges: 0.5-2.0 and 1.0-2.0 μm. Although the table shows concentrations at discrete intervals of time, the recording of data was in real time, permitting the detection of rapping puffs at intervals of about 6 sec every 36 sec (timed for the outlet section of the precipitator) and the detection of concentration changes after changes were made in ammonia injection. In Table 61, the concentrations listed as minimum values were observed between rapping events, and the concentrations listed as maxima were observed during rapping.

The data constituting the third group of experimental data in Table 61 illustrate the delay in the change in fly-ash concentrations emitted from the precipitator after the injection of ammonia was started. These data indicate that the injection of ammonia gradually brought about decreases in the amount of ash emitted from the precipitator during time intervals both between and during rapping events.

The data in Table 61 make it apparent that either with or without ammonia injection the rapping of the electrodes made a highly important contribution to the time-average emission of particulate. Consider the data for particles in the 1.0-2.0 μm size range recorded at 0905 hr without ammonia injection. Taking the minimum concentration of 44 particles/cm^3 to be representative for the 30-sec interval between rapping events and the maximum concentration of 2600 particles/cm^3 to be representative for the 6-sec interval during rapping, one can calculate that the time-average concentration was approximately 400 particles/cm^3 (roughly

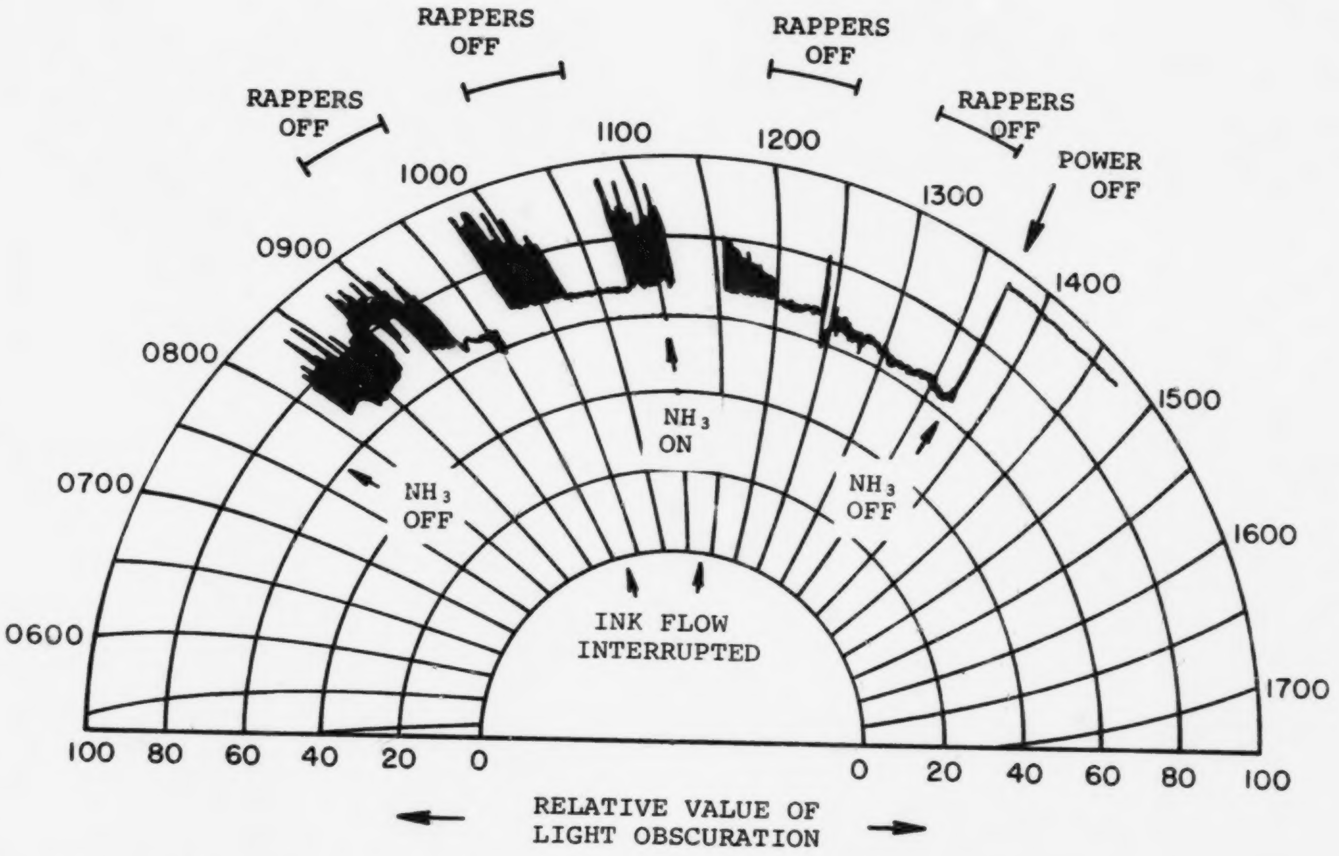

Figure 17. Effects of changes in ammonia injection and electrode rapping on the emission of particulate from Gallatin Precipitator 4C as indicated by the Bailey bolometer (20 ppm of NH_3)

Table 61. EMISSION OF FLY ASH IN VARIOUS SIZE RANGES AS A FUNCTION OF ELECTRODE RAPPING AND AMMONIA INJECTION AT GALLATIN UNIT 4[a]

Injected NH_3 concn, ppm	Electrode rapping	Duration of NH_3 injection, min	Particle concn, no./cm^3, vs. size range			
			0.5-2.0 µm		1.0-2.0 µm	
			Min[b]	Max[b]	Min[b]	Max[c]
0	On	-	1200	>4400	44	2600
0	Off	-	710	-	43	-
20	On	15	610	2700	80	1100
		26	380	2300	<4	38
		38	270	420	<4	38
20	Off[d]	62	250	-	<4	-
		85	250	-	<4	-

[a] Determined with the Climet particle counter.

[b] Recorded during intervals between rapping events in the outlet electrical section.

[c] Recorded during intervals of rapping in the outlet electrical section, repeated approximately every 30 sec.

[d] Discontinued 60 min after the injection of ammonia was started.

10 times the value found without rapping). Similar consideration of data for the 1.0-2.0 µm range recorded at 1138 hr with injection leads to the calculation of a time-average concentration of at least 6 particles/cm^3 (at least 1.5 times the value found without rapping). (The indicated ratio of the time-average concentrations without and with ammonia injection—about 100:1—is not apparent in the Andersen impactor data given in Table 55. There is no apparent explanation for the discrepancy in the Climet and Andersen data).

It was somewhat surprising to find evidence that rapping caused reentrainment of particles in size ranges as low as 0.5-2.0 and 1.0-2.0 µm. It was not expected that the force of rapping could break up agglomerates of particles on the precipitator electrodes to the degree that appreciable concentrations of this fine material would be produced. Admittedly, there is some uncertainty in the actual size limits of the particles counted, particularly the upper size limit. This limit was governed by the properties of the cyclone that was used in the sampling line to prevent large particles from entering the Climet counter. The specified upper limit of 2.0 μm may not be precisely correct, but it should not be in error to a degree altering the conclusion that very fine particles are dispersed and reentrained by electrode rapping.

SECTION VII

DISCUSSION OF CONDITIONING WITH SULFUR TRIOXIDE

Three aspects of the conditioning of fly ash with sulfur trioxide are considered in this section. The first is a practical question: What are the parameters of a power-plant emission system that determine the effectiveness of the conditioning process? The second aspect of sulfur trioxide conditioning involves two theoretical questions: What is the mechanism by which sulfur trioxide is collected by fly-ash particles after the conditioning agent is injected into a flue-gas stream? And what are the mechanisms by which the collected agent conditions the ash and improves its electrostatic precipitation? (From the results of the research described previously in this report, it is apparent that the process of lowering the electrical resistivity is not the only important phenomenon, despite the usual concept to the contrary.) The third subject is posed by this question: What undesirable effects, if any, are encountered during the use of sulfur trioxide for conditioning?

PARAMETERS OF A POWER-PLANT EMISSION SYSTEM THAT AFFECT THE EFFICIENCY OF SULFUR TRIOXIDE CONDITIONING

Source of the Sulfur Trioxide Injected

Three sources of sulfur trioxide as a conditioning agent are discussed in this report:

(1) Anhydrous sulfur trioxide in a stabilized liquid form

(2) Concentrated sulfuric acid as a liquid

(3) A mixture of sulfur dioxide with air passing through a catalytic oxidizer that converts the dioxide to the trioxide

There is a fourth source that is currently receiving consideration: elemental sulfur that is burned to produce the dioxide, which is then catalytically converted to the trioxide in a mixture with excess air. However, the research discussed in this report did not include any experience with sulfur trioxide from elemental sulfur as the ultimate source material.

Other publications have discussed the advantages and disadvantages of the various methods of injecting sulfur trioxide.[3,10] These publications have dealt with such matters as equipment requirements, cost factors, and safety considerations. This report, therefore, is limited to a consideration of the effectiveness of the sulfur trioxide from injection systems based on the first three source materials listed above.

The experimental data give no apparent basis for a choice among the different types of injection systems. The resistivity data indicate that each type of system produced the expected change in the properties of the fly ash. Only in one instance was there evidence of the failure of an injection system to lower the resistivity of fly ash. This failure occurred at Unit 3 of the Cherokee plant, where use was made of one of the two designs of an injection system based on volatilization of sulfuric acid. The failure is attributed to an unidentified flaw in the installation or the operation of the injection system rather than to a basic problem with the design concept.

Experience by personnel of Southern Research Institute in confidential studies of sulfur trioxide conditioning for private industry has shown failures of sulfur trioxide conditioning to produce the expected reductions in fly-ash resistivity in power plants other than the Cherokee plant. Details of these studies cannot be included in this report. However, one of the principal conclusions reached in these studies can be stated here. It is evident that, regardless of the type of injection system used, careful attention must be given to the design of the interface of an injection system with the flue-gas stream. The design must permit efficient mixing of the stream of concentrated sulfur trioxide in carrier gas with the large excess of flue gas. If the mixing is inefficient, sulfur trioxide will combine with water vapor and undergo condensation as a mist of sulfuric acid and, as a consequence, it will not be collected uniformly on the surfaces of individual fly-ash particles. The unwanted phenomenon of acid condensation may be difficult if not impossible to avoid completely. Even so, it apparently has been avoided or minimized more successfully in some installations of injection systems than in others.

Site of Sulfur Trioxide Injection

Three sites of sulfur trioxide injection in the train leading flue gas from the boiler of a power plant to the stack have been investigated. One site is upstream from the mechanical collector (cyclone) in a system for gas cleaning comprised of both the cyclone and an electrostatic precipitator. Another site is the duct immediately upstream from the precipitator in a plant where no mechanical collector is used. The third site is the duct between a mechanical collector and a precipitator.

Conditioning of fly ash apparently can be successful in plants with all of the locations of sulfur trioxide injection. Deposition of part of the sulfur trioxide on the larger fly-ash particles that were subject to mechanical removal did not prevent sufficient deposition on the smaller particles removed by electrostatic precipitation. Presumably, the smaller surface area of the larger particles was the predominant factor in ensuring adequate conditioning of the smaller particles.

Another site of sulfur trioxide that might be used is the gas duct upstream from the air preheater, in which the temperature of the flue gas is lowered from about 300°C to the customary range around 150°C at the inlet of the electrostatic precipitator. This site upstream from a preheater has been seldom used, although it offers the theoretical advantages of a temperature high enough to avoid loss of sulfur trioxide by acid condensation and a longer time of contact between the conditioning agent and the fly ash (more nearly simulating the conditions of contact between the naturally produced gas and the ash). Injection of sulfur trioxide upstream from the air preheater may lead to acid corrosion of the cold-side surfaces of the preheater, but it is questionable whether the injection of the gas would cause a greater problem than the natural occurrence of the gas at concentrations associated with medium- and high-sulfur coals. Watson and Blecher[14] are among the few investigators who have used high-temperature injection upstream from an air preheater. Their results were unfavorable, but the reason for the lack of success is not known.

Concentration of Sulfur Trioxide Injected

A graph showing the results of resistivity determinations as a function of the concentration of sulfur trioxide injected in various power plants is given in Figure 18. The several power plants are denoted in this figure by the numbers that were listed previously in Table 1.* Also, the gas temperatures at which the precipitators operated are shown in the figure. Information about still other parameters that are assumed to be pertinent to the relationship between resistivity and injected concentration of sulfur trioxide is listed below:

Plant	Gas Cleaning	pH of ash
2	Mechanical and electrostatic	7.0
3	Electrostatic only	11.0
5	Mechanical and electrostatic	11.1
6	Electrostatic only	8.1
7	Electrostatic only	4.8

The pH values listed above are equilibrium values of ash-water slurries.

Different curves are plotted in Figure 18 for the five plants represented. Only two curves portraying the data for one group consisting of Plants 3, 5, and 6 and another group consisting of Plants 2 and 7 could be constructed to represent the experimental data if the uncertainty in the measured values of resistivity were one order of magnitude, which may be justifiably assumed. However, any effort to limit the number of correlations for the different plants is probably not warranted because of the wide variations in the parameters listed.

One of the principal conclusions warranted from Figure 18 is that for fly ash with a resistivity of around 1×10^{12} ohm cm prior to conditioning an injected concentration of 15 to 20 ppm of sulfur trioxide was sufficient to lower the resistivity to an acceptable value of 1×10^{10} ohm cm. Another major conclusion is that for fly ash with a normal resistivity of about 1×10^{11} ohm cm or less, an injected concentration of only 5 ppm of sulfur trioxide would have been adequate.

It is debatable whether the fly ash at Plant 7 (the Bull Run plant), which had the lowest resistivity prior to conditioning (between 1×10^{10} and 1×10^{11} ohm cm), was in need of a reduction in resistivity to improve its electrostatic

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*Those plants for which names can be specified are as follows: Plant 2, Cherokee Unit 2; Plant 5, Arapahoe Unit 4; Plant 7, Bull Run Unit 1 (Collector 1B).

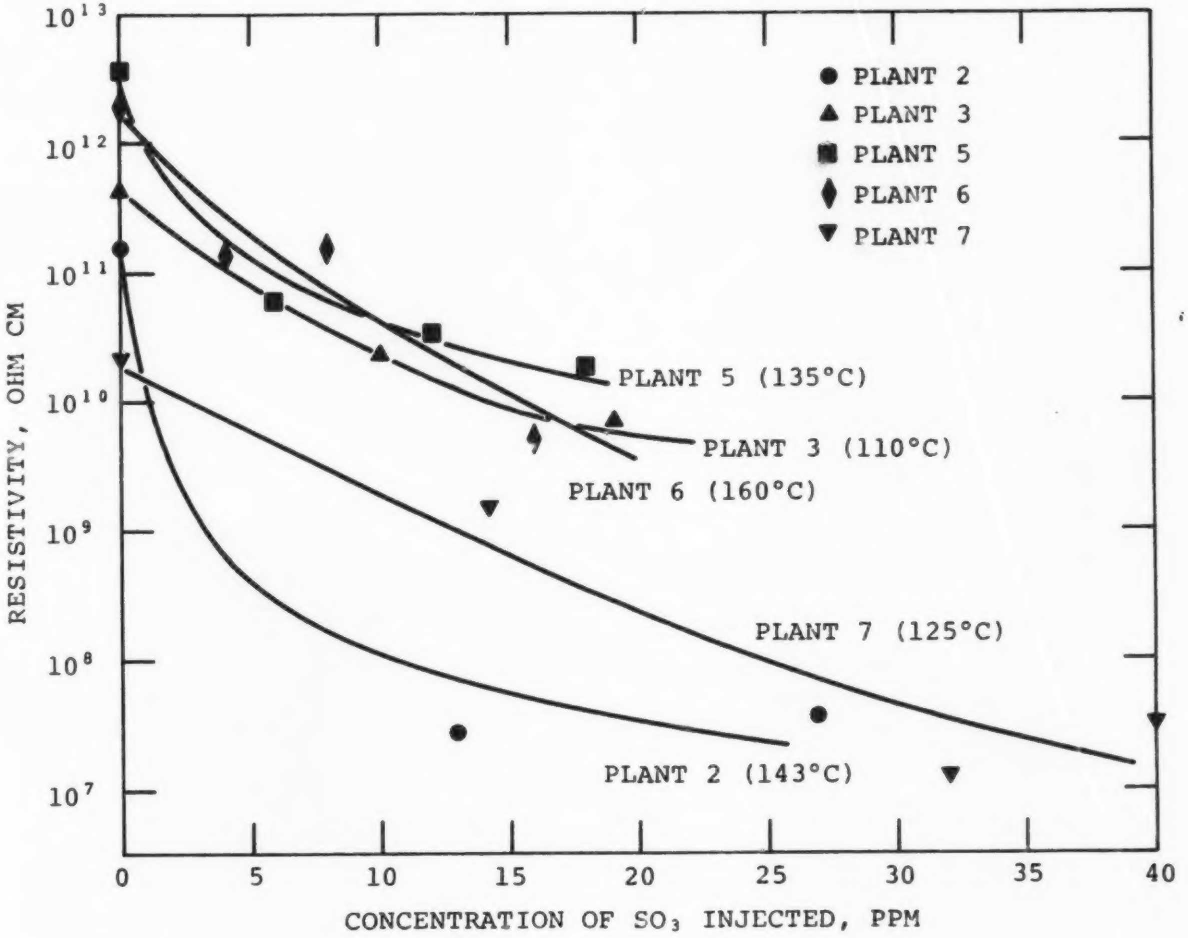

Figure 18. Resistivity as a function of the concentration of injected sulfur trioxide

precipitation. If the values of resistivity of unconditioned ash that were measured at this plant on two separate occasions are valid, they are low enough to indicate that the factor limiting precipitation efficiency was something other than the resistivity. If, on the other hand, the precipitator electrical data obtained on one occasion (Figure 5) are taken into account, one concludes that lowering of the resistivity was helpful. However, a discrepancy between two sets of electrical data (Figures 5 and 7) further complicates the interpretation of the effects of the conditioning process. (An effort to interpret the effects of conditioning of the Bull Run plant in terms of a mechanism other than the lowering of resistivity is given later on pages 128 through 131).

Chemical Properties of the Fly Ash

Even though the chemical composition of the fly ash treated in various power plants varied widely, all of the fly ash was susceptible to conditioning with sulfur trioxide. This conclusion is apparent from the resistivity data plotted in Figure 18. Still, the conclusion given earlier, that the required concentration of sulfur trioxide varies from one ash to another, must be kept in mind.

One aspect of the chemistry of fly ash that appears to be related to the conditioning process is the change in the concentration of sulfate on the surface of the ash with conditioning. Resistivity data for conditioned and unconditioned ash are shown in Figure 19 as functions of the concentration of sulfate dissolved in aqueous slurries. The data in this figure can be used to discuss two questions: (1) Does the quantity of sulfate on unconditioned ash give an indication of the magnitude of resistivity and the need for conditioning? (2) Does the quantity of sulfur trioxide added to the ash during conditioning give an indication of the success in lowering resistivity?

The apparent answer to the first question is negative. The two ashes with the highest concentrations of sulfate prior to conditioning had resistivities of about 2×10^{11} and 4×10^{12} ohm cm. The fact that these ashes were the only ones collected between mechanical and electrostatic dust collectors, which caused them to have the highest area-to-mass ratios, is the probable cause of their high sulfate concentrations.

The apparent answer to the second question is also apparently negative. The ash from Plant 5 (Arapahoe Unit 4) required a much larger increment in sulfate concentration than any of the other materials to reach a resistivity value of around 1×10^{10} ohm cm. The behavior in this ash is attributed to

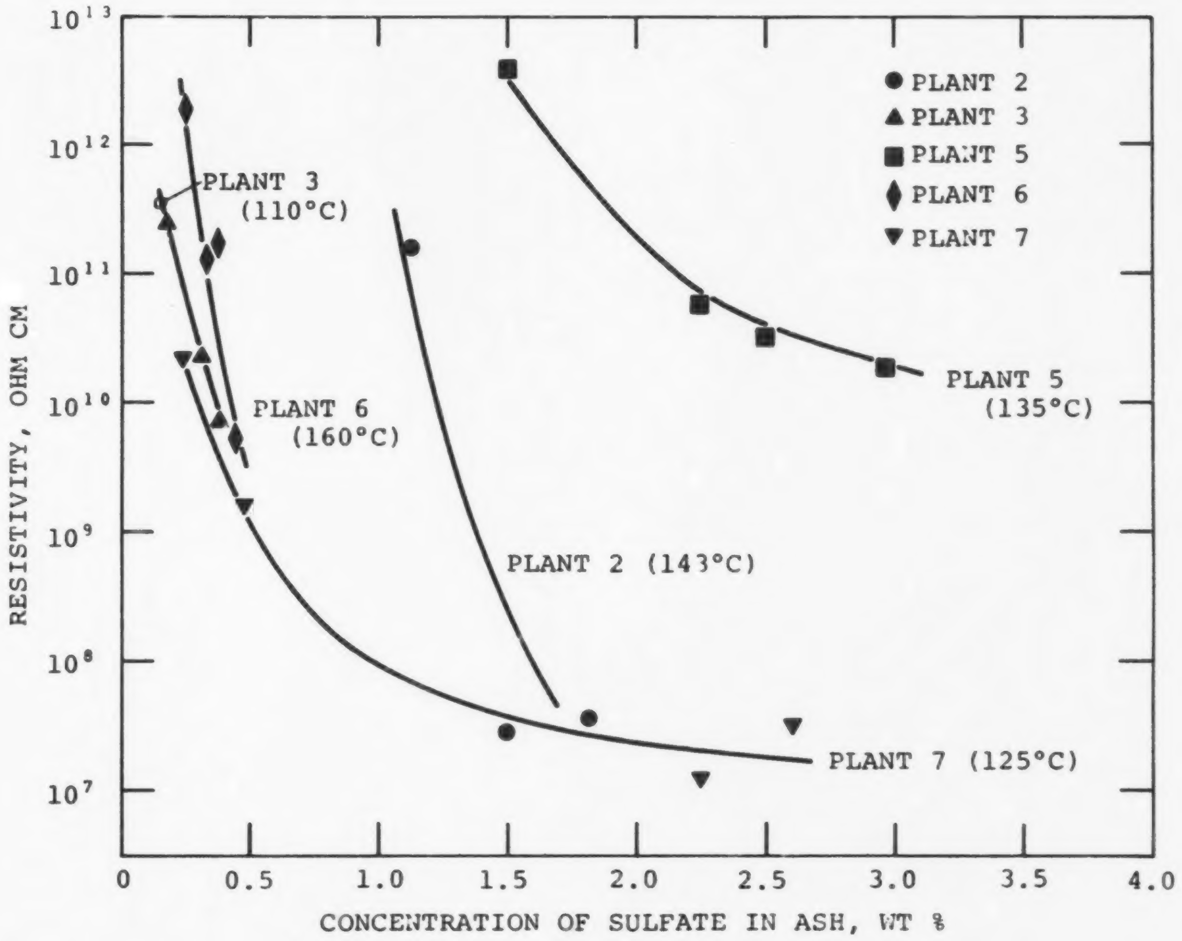

Figure 19. Resistivity as a function of the sulfate concentration in fly ash

the highly basic nature of the material, which resulted in conversion of much of the collected sulfur trioxide to a salt (perhaps calcium sulfate) that was not of low intrinsic resistivity.

Temperature of the Flue Gas

Fly ash was successfully conditioned with sulfur trioxide at gas temperatures ranging from a maximum of 160°C to a minimum of 110°C. It is noteworthy that successful results were obtained at 160°C despite the fact that this temperature was too high to permit the collection of sulfur trioxide by the process of condensation and the neutral quality of the ash was not favorable to base-induced adsorption of sulfur trioxide. It is noteworthy also that at the other extreme of temperature, 110°C, the addition of sulfur trioxide was effective even though at such a low temperature the conditioning of fly ash by the water vapor in the flue gas is greatly facilitated. In other words, at the low temperature the effect of a small concentration of added sulfur trioxide was readily apparent in competition with the effect of the far higher concentration of water vapor.

MECHANISMS OF COLLECTION OF SULFUR TRIOXIDE ON FLY-ASH PARTICLES

There are at least two distinctly different mechanisms by which sulfur trioxide in flue gas can be collected on the surfaces of fly-ash particles. One mechanism is the condensation of a mixture of sulfur trioxide and water vapor, with fly-ash particles serving as condensation nuclei. This phenomenon results in the formation of a liquid layer on the particles; however, it can occur only if the temperature is below the dew point of the vapors existing in the duct. Other mechanisms involve the adsorption of sulfur trioxide and probably the concurrent adsorption of water as well. As discussed subsequently, different mechanisms of adsorption may exist, depending upon the sequence in which sulfur trioxide and water are adsorbed.

Acid Condensation

The phenomenon of acid condensation can be critically analyzed only if reliable thermodynamic data exist for predicting dew points of mixtures of sulfur trioxide and water vapor or if reliable experimental data exist for showing dew points of adequately analyzed vapor mixtures.

Two notable attempts to secure the necessary thermodynamic data for predicting dew points have been made. The first of these two efforts was reported by Müller in 1959[30] and was based on data previously compiled by Greenewalt[39] and Abel;[40] the second effort, reportedly with the advantage of more accurate background data, was reported by Gmitro and Vermeulen in 1963[31] and 1964[41] and later summarized by Snowdon and Ryan in 1969.[42] Dew points predicted from the original work of Greenewalt and Abel and the later work of Gmitro and Vermeulen are shown in Figure 20 for various concentrations of sulfuric acid at two different concentrations of water, 8 and 10% (covering the usual range found in flue gases produced in coal-burning plants) for an assumed total pressure of 1 atm.* The curves in Figure 20 show that at a given set of sulfur trioxide and water vapor concentrations the dew point predicted by the data of Greenewalt and Abel is about 15°C higher than the value predicted by the data of Gmitro and Vermeulen. They also show that at a given sulfur trioxide concentration the dew point predicted by either source of data decreases about 3°C as the concentration of water vapor is lowered from 10 to 8%.

Numerous experimental efforts have been made to determine dew points of mixtures of sulfur trioxide and water vapor of known compositions. One of the most recent and perhaps the most reliable study was reported by Lisle and Sensenbaugh.[43] The results of this study indicate that the dew-point curves based on the work of Greenewalt and Abel are more accurate than those based on the work of Gmitro and Vermeulen, despite the access of the latter authors to more up-to-date reference data.

To predict the possibility that acid condensation may have occurred in the several plants where sulfur trioxide was used as a conditioning agent, the range of reported concentrations of the agent in each plant is shown by data points along a horizontal dashed line in Figure 20. The conclusion reached by comparing the locations of the dew-point curves is that only the temperature at Plant 3 was clearly below the dew point at all injected concentrations of conditioning agent. The possibility that the temperature at Plant 5 or Plant 7 was below the dew point at the two higher concentrations of conditioning agent cannot be excluded; however, the temperature at Plant 5 was definitely above the dew point at the lowest concentration of the agent, which gave evidence of a marked reduction in resistivity. Finally, the possibility that the temperature in either Plant 2 or Plant 6 was ever

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*Recalculation of dew points from the data of Greenewalt and Abel was made, since the results of Müller's calculations from these data cannot be easily seen from Müller's graphical summary.

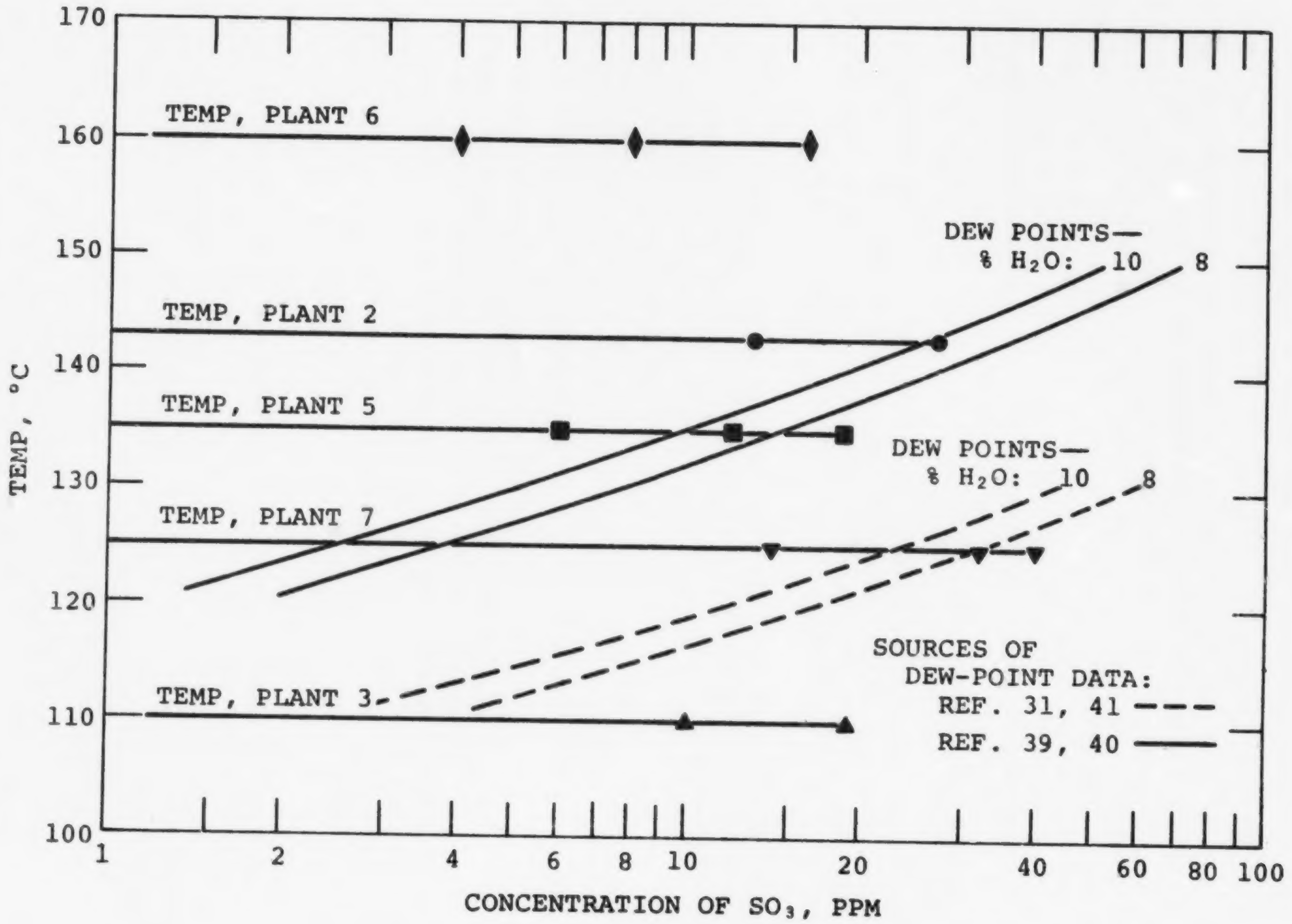

Figure 20. Dew points of vapor mixtures of sulfur trioxide and water

below the dew point can be completely excluded, assuming that the possible locations of the dew points cannot be outside the range indicated by the curves in the figure.*

The above conclusions indicate, at least, that condensation of acid is not necessary for the conditioning of fly ash by sulfur trioxide. Although condensation may have been involved in the conditioning process at Plant 3, it did not necessarily occur; if chemisorption of the sulfuric acid on the highly basic ash occurred more rapidly than the condensation process, the concentration of sulfuric acid vapor could have been lowered to levels below the minimum required for condensation.

Acid Adsorption

The above consideration of the condensation mechanism leads to the conclusion that acid adsorption is at least a sufficient mechanism, if not a necessary mechanism, for fly-ash conditioning in the presence of sulfur trioxide.

The pioneering work by Chittum[8] led to the conclusion that conditioning of fly ash by an acidic vapor involves, first, the chemisorption of this vapor on the fly ash and then enhanced adsorption of water vapor on the chemically altered surface of the fly ash. Chittum argued that a strongly basic ash would have a greater affinity for an acidic vapor (such as sulfur trioxide) than a neutral or acidic ash and, thus, a strongly basic ash should be most easily conditioned.

The results of our work appear to be inconsistent with Chittum's hypothesis. This point can be supported by the data obtained in the studies at Plants 2 and 5. The ash at Plant 5 was more basic than that at Plant 2 and, moreover, was conditioned at a slightly lower temperature. In view of the differences in the conditioning parameters, the Chittum hypothesis would predict more efficient conditioning of the ash at Plant 5. The experimental data show that more efficient conditioning occurred with the ash at Plant 2, whether the criterion of effectiveness is based on the lowering of resistivity observed with a given rate of injection of conditioning agent or the lowering of resistivity observed with a given amount of agent collected as sulfate on the ash.

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*In the above discussion, the fact that the total pressure was not precisely 1 atm in all of the plants is ignored. In Plants 2 and 5 (located in the Denver area), the total pressure was only about 0.83 atm. However, the conclusions reached above would not be significantly altered by making a correction for the difference in pressures.

Additional data contrary to the Chittum hypothesis were obtained at Plant 6, where the resistivity was lowered markedly with either a low rate of injection of conditioning agent or a small amount of agent collected on the ash, despite the near neutrality and high temperature of the unconditioned ash (two factors that were unfavorable for chemisorption).

The studies described in this report indicate that a highly basic ash will require more acid conditioning agent than a neutral ash, in terms of either the concentration injected in the duct or the concentration collected in the ash, for the following reasons: (1) the acid initially collected is not simply adsorbed but it undergoes reaction with basic components of the ash, such as calcium oxide, to form sulfate salts, such as calcium sulfate, that may have little affinity for water; (2) the amount of acid collected must increase to the point that an adequately thick protective layer of sulfate salts covers the remaining basic components of the ash and the amount of acid collected thereafter can exist on the surface of the ash in the form of sulfuric acid rather than as sulfate salts; (3) the layer of sulfuric acid ultimately produced exhibits a strong affinity for water and, thus, a layer consisting of both sulfuric acid and water with the necessary electrical conductivity is finally produced on the surface of the ash.

The fact that only a small amount of collected sulfate was apparently required to condition the highly basic fly ash at Plant 3 appears, on initial consideration, to be inconsistent with the theoretical concepts outlined in the preceding paragraph. One possible rationale for the apparent discrepancy was that conditioning in Plant 3 occurred at an unusually low temperature, where the rate of diffusion of sulfuric acid through the initially produced layer of sulfate salts would be relatively low and, thus, the required thickness of the protective layer of sulfate salts would be reduced.

MECHANISM OF SURFACE CONDUCTION ON FLY ASH CONDITIONED WITH SULFUR TRIOXIDE

It is reasonable to assume that the predominant conductive material on fly ash conditioned with sulfur trioxide is sulfuric acid, occurring as a surface film that may be only a few molecular layers thick. The assumed predominance of sulfuric acid as the conductive material is consistent with the behavior of this substance as a component of bulk aqueous solutions. The assumed role of sulfuric acid is also consistent with certain observations made by Southern Research Institute in studies of the pH behavior of fly ash in aqueous slurries.

In aqueous solutions, the conductivity of sulfuric acid and other strong acids is attributable to the high apparent mobility of hydrogen ions that are formed by ionization of the acids. The mobility of hydrogen ions is so great in comparison with the mobility of other singly-charged cations that the electrical migration of hydrogen ions is explained in terms of a unique phenomenon termed the "proton-jump" process.[44] In this process, the transfer of charge occurs along a chain of hydrogen ions and water molecules, rather than by the direct migration that is required for other cations such as sodium and potassium ions.

For the studies of the pH behavior of slurries of fly ash and water discussed in this report, the major emphasis has been placed on the pH values reached at equilibrium or steady state. However, auxilliary experiments on the pH behavior of fly-ash slurries, as described in a previous report,[22] revealed that equilibrium pH values often do not give a true indication of the acid-base composition of substances residing on the outermost surfaces of fly-ash particles. A fairly common experimental result was the finding that, immediately after contact was made between fly ash and water, the pH decreased to values in the acid range at least momentarily, even though the pH sometimes increased subsequently to equilibrium values in the alkaline range. This result was attributed to the existence of (1) a discrete surface layer of sulfuric acid, which dissolved rapidly to give the initial acidic pH values, and (2) an excess of soluble base toward the interior of the fly-ash particles, which neutralized the surface acid by a slower process of dissolution. Additional experiments involving the treatment of fly ash with ethanol rather than water gave further evidence of the occurrence of sulfuric acid as a surface material.[22] Treatment with ethanol rather than water was apparently a successful means of dissolving the surface acid without dissolving the interior base.

It may be necessary to revise the present concept of sulfuric acid as the predominant conductor of electricity on conditioned fly ash on the basis of an investigation of surface-conduction processes being conducted by Bickelhaupt of Southern Research Institute.[45] In a preliminary report, Bickelhaupt has stated that alkali-metal ions, especially sodium ion, carry a large fraction of the current over the surfaces of fly-ash particles. His conclusion is based on results obtained with a laboratory environment, where temperatures range from about 100°C to 150°C and water vapor is maintained at concentrations of 9%-volume in an atmosphere of air surrounding the fly ash. In later work, sulfur trioxide will be added to the gaseous environment and the contribution of alkali-metal ions will be reexamined. However, on the basis of preliminary data, Bickelhaupt has suggested that sulfur trioxide conditioning may lead primarily to a process in which alkali-metal ions are released from the glassy matrix of fly ash and the numbers of these ions available to conduct electricity are thereby increased.

MECHANISM OF CONDITIONING BY SULFUR TRIOXIDE THROUGH EFFECTS OTHER THAN LOWERING OF ELECTRICAL RESISTIVITY

Increasing the Cohesiveness of Fly-Ash Deposits on Precipitator Electrodes

Different investigators[15,46] have emphasized the importance of the cohesiveness of fly-ash particles in maintaining the physical integrity of the deposits and avoiding excessive dispersal and reentrainment of individual particles and agglomerates during electrode rapping. For fly ash of high electrical resistivity, cohesive forces are not essential, for the high electric field that can be maintained through deposits of this material will restrain losses by rapping reentrainment. For fly ash of low resistivity, on the other hand, cohesive forces are essential, for the restraining force of the electric field is not adequate.

Dalmon and Tidy[15] have conducted experiments in which the two mechanisms of sulfur trioxide conditioning (decreasing resistivity and increasing cohesiveness) were apparent. The results obtained by these investigators showed that the electrostatic precipitation of fly ash with an inherent high resistivity was improved by sulfur trioxide through its effect on resistivity. The results showed, on the other hand, that the precipitation of fly ash with a low resistivity (caused by the presence of a large amount of conductive carbon particles) was improved by sulfur trioxide through the increased cohesiveness of fly-ash particles.

Studies of sulfur trioxide conditioning at the Bull Run plant, as described in this report, lead to the conclusion that the predominant mechanism of conditioning was increased cohesiveness. The resistivity of the unconditioned ash was not abnormally high. Furthermore, the fact that the resistivity was lowered by conditioning is not necessarily proof of the importance of this process; indeed, the lowering of resistivity as the sole effect of conditioning might have led to a lower efficiency of precipitator operation through enhanced reentrainment losses. The evidence for conditioning through increased cohesiveness is admittedly indirect; even so, this evidence, especially as obtained during the second of the two investigations at the Bull Run plant (July 1974), is worthy of consideration. First, precipitation efficiency was increased despite the possibility that increased reentrainment losses might have resulted from lowered resistivity. Second, light-obscuration data obtained with the Lear-Siegler instrument gave distinct evidence of reduced rapping-puff intensity. Third, several visual observations were indicative of increased cohesiveness, as follows:

- With conditioning, the ash collected in alundum thimbles during precipitator efficiency determinations adhered more or less uniformly to the entire gas-filtration area; without conditioning, the ash did not adhere to the filtration area but fell into the bottom of the thimble.

- With conditioning, sampling pipes and other experimental devices inserted into the gas duct were densely coated with fly ash on surfaces facing the gas flow. The devices inserted in the colder side of the duct (where the uptake of sulfur trioxide by the ash was more efficient) were more densely coated with ash than the devices inserted at the higher gas temperatures. The ash was held tenaciously to all collection surfaces, not being removed simply by brushing but being removed only by vigorous scraping. Without conditioning, coatings were comparatively light and more easily removed.

- Thicknesses of ash deposits on the precipitator electrodes are characteristically greater with conditioning than without conditioning. (This statement is based on observations made by TVA personnel during periodic outages, which have allowed direct inspections of the electrodes.)

Finally, as evidence of increased cohesiveness, there is the occurrence of the "snow-flake" phenomenon: the deposition of large agglomerates of fly ash in the area underneath the plume. (The snow-flake phenomenon is discussed later in this report in the context of undesirable manifestations of sulfur trioxide conditioning.)

Altering the Conductive Properties of Flue Gas

The pronounced effect of ammonia conditioning on the conductive properties of flue gas (the "space-charge" effect) has been demonstrated in several power plants, as previously described in this report. A similar effect of sulfur trioxide conditioning may also occur through one of the following two processes:

- Ionization of the molecules of sulfuric acid introduced by sulfur trioxide injection

- Ionization of small droplets of condensed sulfuric acid introduced when the injected sulfur trioxide is below the dew point.

No direct evidence for either process was obtained during the studies described in this report. However, some of the results obtained at the Bull Run plant point to the possible significance of one or both of these effects. These results are discussed below; however, the two phenomena are discussed first from a theoretical point of view.

It is possible that the ionization of molecules of sulfuric acid may take precedence over the ionization of molecules of other electronegative gases. It has been clearly established by studies of the ionization of air[47] that the addition of electronegative gases such as water vapor or sulfur dioxide in the region of a negative corona causes a transfer of electrons to the more electronegative species, producing less mobile charge carriers and increasing the voltage required for electrical breakdown of the gaseous mixture. The occurrence of charge transfer from oxygen molecules to sulfur dioxide molecules, for example, depends upon the relative affinities of the two gases for electrons and the relative concentrations of the two gases.

It is not certain that the electronegativity of sulfuric acid molecules would be sufficiently great to permit an extensive transfer of charge to these molecules from other types of molecules. With the concentration of sulfuric acid at a typical value of about 10 ppm and the concentration of sulfur dioxide at a typical concentration in excess of 500 ppm, the electronegativity of sulfuric acid would have to be very high indeed, relatively speaking, to permit the transfer of charge to occur extensively. Unfortunately, there do not appear to be any experimental data available at present from which the efficiency of process can be estimated.

At least the feasibility of selective ionization of sulfuric acid molecules can be evaluated, however, by comparing the concentration of these molecules with the concentration of gaseous ions occurring in an electrostatic precipitator. A concentration of 10 ppm of sulfuric acid corresponds to a molecular concentration of 1.73×10^{14} molecules/cm^3 (calculated for 150°C and 1 atm). A corona current density of 20 nA/cm^2 at an electric field of 3 kV/cm in the gas stream within a precipitator corresponds to an ionic concentration of 1.97×10^7 ions/cm^3 (calculated for the same temperature and pressure, with an assumed ion mobility of 2.2 cm^2/(volt sec)). Thus, although the concentration of sulfuric acid is low in comparison with the concentrations of other flue-gas components, its ratio to the concentration of gaseous ions is of the order of 1 x 10^7. Hence, it is at least theoretically possible for the sulfuric acid molecules to assume all of the charge carried by ions and, as a result of their mass and size, to reduce substantially the effective mobility of gaseous ions. One of the practical effects of sulfur trioxide conditioning, therefore, may be a space-charge effect analogous to that produced by ammonia conditioning.

It may be more easily seen how a mist of sulfuric acid can produce a space-charge effect. If injected sulfur dioxide is partly condensed as an acid aerosol of small particle size, transfer of charge from gaseous ions to be aerosol particles would have a pronounced space-charge effect, analogous to that attributed to ammonium sulfate or bisulfate particles during ammonia conditioning.

What practical reason is there for presenting the foregoing arguments about a space-charge effect from sulfur trioxide conditioning? During the studies described in this report, only one type of experimental information was obtained to suggest the need for considering the possibility of a space-charge effect. This information was obtained during the second investigation of sulfur trioxide conditioning at the Bull Run plant (July 1974) when the precipitator voltage currents with and without sulfur trioxide injection were compared as shown in Figure 7. The effects of injection—increasing the voltage required for a given current density or decreasing the current density at a given applied voltage—at least suggest the occurrence of a space-charge effect in view of the fact that no apparent change occurred in fly-ash resistivity.

DELETERIOUS EFFECTS OF SULFUR TRIOXIDE CONDITIONING

Stack Losses of Sulfur Trioxide

It is sometimes claimed that injected sulfur trioxide is quantitatively collected on fly ash and none of the vapor escapes to the stack and thence to the atmosphere.[10] Under some circumstances, this claim appears to be justified. For instance, with high-alkalinity ash as studied at the Arapahoe plant, little of the injected conditioning agent was found in the flue gas entering the precipitator, and little if any would be expected at the outlet. Under other circumstances, the claim of no stack loss of injected sulfur trioxide must be challenged. For example, with low-alkalinity ash at Plant 6, a substantial fraction of the agent was found as vapor at the precipitator inlet. In view of the finding by Cuffe *et al.*[48,49] of roughly equal concentrations of naturally occurring sulfur trioxide at precipitator inlets and outlets, no appreciable removal of the injected vapor would be expected within the precipitator at Plant 6 or other plants with similar circumstances. Finally, with weakly acidic ash at the Bull Run plant, the study in July 1974 showed that roughly one-third of the injected sulfur trioxide remained in the gas stream at both the inlet and the outlet of the precipitator.

In view of the increasing concern about the toxicity of sulfate particulates, it is important to regulate the rate of sulfur trioxide injection to minimize loss to the stack. One state (West Virginia) actually prohibits sulfur trioxide conditioning to avoid the problem. This extreme position may not be justifiable. Even so, it is clear that further research is needed to define the acceptable amount of stack loss. Also, further research is needed to define the concentrations of injected sulfur trioxide under various power-plant circumstances that will permit the desired degree of conditioning to occur without allowing an unacceptable stack loss.

Fallout of Large Fly-Ash Aggregates from a Power-Plant Plume

Currently, this phenomenon is the cause of considerable annoyance at the Bull Run plant, where it is referred to as "snow flaking." With injected concentrations of sulfur trioxide of the order of 20 ppm, which are found to give the best improvement in precipitator performance, fallout of large fly-ash aggregates in the vicinity of the plant causes complaints from the plant personnel and the residents of the area around the plant.

The snow-flake problem was observed during the investigation at the Bull Run plant in July 1974, and an effort was made to determine the factors that contribute to the problem. Direct observations and information obtained from the plant personnel indicate that the fallout of slow flakes is more severe under conditions of high ambient humidity, which occur at night or in early morning. Consideration was given to possible origins of the material: (1) reentrainment from the precipitator electrodes or the walls of the outlet duct and the stack and (2) formation of aggregates of fly ash within the plume issuing from the stack. The apparent relationship of the problem to ambient conditions suggests formation in the plume. Also, observations that the surfaces of individual aggregates are rounded rather than flat before impact of the material on the ground suggest formation in the plume. If reentrainment were the origin of the material, flat surfaces prior to impact would be expected. Actually, the deposited particles always have flat surfaces against the plane of impact, but such surfaces appear to be produced only during impact. The final conclusion was that aggregation occurred in the plume as the direct result of condensation of excess sulfur trioxide in the presence of high moisture levels, with the resulting increase in cohesive forces between fly-ash particles.

It is ironic that the flake problem becomes severe when the concentration of injected sulfur trioxide reaches the optimum level for good precipitator performance. Unfortunately, it is not possible to recommend any measure that would overcome the problem, at least not on the basis of information presently available. A worthwhile task in further research would be to survey power plants using sulfur trioxide conditioning to determine how common the problem is and to make an effort to deduce more definitely what factors contribute to the difficulty.

SECTION VIII

DISCUSSION OF CONDITIONING WITH AMMONIA

As in the instance of fly-ash conditioning with sulfur trioxide, there are both practical and theoretical questions associated with the use of ammonia as an alternative agent that require discussion. These questions are similar to those dealt with in the preceding discussion of sulfur trioxide. What are the circumstances in a power plant that permit ammonia to be used effectively? What are the mechanisms of conditioning by ammonia? What disadvantages are associated with ammonia conditioning?

PARAMETERS OF A POWER-EMISSION SYSTEM THAT AFFECT THE EFFICIENCY OF AMMONIA CONDITIONING

Fly Ash from Low-Sulfur Coals

For treating fly ash from low-sulfur coals, ammonia conditioning was investigated under more limited circumstances than sulfur trioxide conditioning. Thus, it is difficult to give a thorough discussion of the power-plant parameters that affect the efficiency of ammonia conditioning. Moreover, it is difficult to compare ammonia and sulfur trioxide as conditioning agents in plants burning low-sulfur coals because of the lack of opportunities to make direct experimental comparisons under essentially identical circumstances.

On the basis of direct experience, it can be stated that ammonia conditioning produced desirable results in two power plants burning Eastern coals containing about 1% sulfur. In these plants, the fly ash had moderate to moderately high electrical resistivities (about 3×10^{10} to 3×10^{11} ohm cm) at gas temperatures around 130°C. Moreover, the fly ash was mildly acidic, and the flue-gas stream contained naturally produced sulfur trioxide at concentrations of about 2 to 5 ppm. Under these conditions, ammonia conditioning had no apparent effect on the resistivity of the fly ash, but it did produce a marked enhancement of the electric field in the interelectrode space of the precipitator through a space-charge effect.

As demonstrated by precipitator efficiency data obtained with and without conditioning, the practical results of ammonia conditioning were decidedly favorable in one plant (Widows Creek Unit 7). Practically speaking, the results in the second plant (Bull Run Collector 1C) were not fully assessed, for no comparative determinations of precipitator efficiencies were made with and without conditioning. However, TVA regarded the results of ammonia conditioning as relatively unsuccessful on the basis on light-obscuration data obtained with the Bailey bolometer and on the basis of the electrical behavior of the precipitator, which was characterized by intensive sparking during the injection of ammonia.

Because of the similarity in the circumstances at the two plants and the parallel in the mechanistic aspects of ammonia conditioning in both plants, it is important to attempt to give an explanation of the apparent difference in precipitator performances. The space-charge effect of ammonia at the Bull Run plant was undoubtedly the direct cause of intensive sparking; however, if the power-supply controls had operated more satisfactorily, they should have been able to suppress the intensity of sparking. Another factor of possible importance at the Bull Run plant in addition to unsatisfactory performance of the power supplies was electrode misalignment. In the inlet section of the Bull Run precipitator, the onset of sparking during ammonia injection occurred at a voltage around 35 KV and an average current density below 10 nA/cm^2. In the corresponding section of the Widows Creek precipitator, the onset of sparking during injection did not occur until the voltage exceeded 40 kV and the average current density approached 40 nA/cm^2. The Bull Run precipitator admittedly has a narrower designed wire-to-plate spacing (11.4 cm) compared with the Widows Creek precipitator (12.7 cm). However, the difference in design spacings seems an unlikely explanation for the pronounced difference in electrical data, and a significant distortion from the design spacing in the Bull Run precipitator seems to be a more likely explanation. In summary, it does not appear reasonable to attribute the lack of success of ammonia conditioning at the Bull Run plant to a fundamental shortcoming in the mechanism of conditioning.

Studies at the Bull Run plant provided the only data for ammonia and sulfur trioxide as alternative conditioning agents under essentially the same circumstances. It does not appear that even at this plant a meaningful comparison of the two agents can be made, largely because of the practical problem of sparking with ammonia conditioning as discussed in the preceding paragraph. Clearly, however, the two agents performed by quite different mechanisms: ammonia through the space-charge effect in the interelectrode space and sulfur trioxide by lowering the resistivity of the fly ash (and perhaps both by increasing the cohesiveness of the ash). The conclusion reached by TVA was that more successful results were obtained with sulfur trioxide; hence, the decision was made to dismantle the ammonia system and install an enlarged sulfur trioxide system.

It is possible only to make conjectures about how ammonia would perform as a conditioning agent for fly ash from low sulfur Western coals, for which sulfur trioxide was directly investigated in a number of power plants. Circumstances in these plants differ from those in which ammonia was studied experimentally in the following ways:

- Sulfur in the coal, typically nearer 0.5% than 1.0%
- Resistivity of the fly ash, usually higher than the values for ash treated with ammonia
- Alkalinity of the fly ash, usually higher than that of the ash treated with ammonia (creating a favorable environment for the collection of sulfur trioxide but a hostile environment for the adsorption of ammonia)
- Sulfur trioxide concentration produced naturally in the flue gas, lower than that in the plant where ammonia was injected (making the reaction of ammonia to produce the space-charge effect more unlikely)

Although any conjectures that can be made about the effects of ammonia conditioning under the different circumstances outlined above may be misleading, a tentative estimation of the utility of ammonia conditioning under these circumstances is given in a later discussion of conditioning mechanisms (pages 138 through 141).

Fly Ash from High-Sulfur Coals

As an aid in improving the collection of fly ash from high-sulfur coals, ammonia conditioning clearly appears to be of value as demonstrated by investigations at the Widows Creek and Gallatin plants. The mechanism does not appear to involve the resistivity of the ash, but it appears instead to consist of a space-charge effect and an increase in the cohesiveness of the ash. The latter two conditioning mechanisms may lead not only to improved collection of fly ash but to elimination of part of the sulfur trioxide gas that is condensed to sulfuric acid mist when flue gas is evolved to the atmosphere and thus cooled to a temperature below the acid dew point. The theoretical aspects of the two alternative conditioning mechanisms and the environmental impact of ammonia conditioning in power plants burning high-sulfur coals are discussed further in the remainder of this report.

MECHANISMS OF AMMONIA CONDITIONING

Alteration of the Electrical Resistivity of Fly Ash

Data on the electrical resistivity of fly ash presented earlier in this report indicate that ammonia conditioning had no clear-cut effect on this property of the ash under the particular circumstances investigated. Treatment of fly ash in two plants burning low-sulfur coals did not produce a measurable reduction in resistivity, contrary to the result tentatively expected. Treatment of ash in two plants burning high-sulfur coals did not produce a measureable increase in resistivity, contrary to the hypothesis suggested previously.[5] (Some of the data for the ash from high-sulfur coals indicated a possible lowering of resistivity—an unwanted effect—but the evidence for lowered resistivity was not conclusive).

As stated previously in the summary of other work on ammonia conditioning (Section III), some investigators in the past have failed to observe changes in resistivity with ammonia conditioning. On the other hand, other investigators have reported significant changes in resistivity (sometimes increases and sometimes decreases, depending upon circumstances). Whether the observed changes were real effects or spurious experimental phenomena cannot now be ascertained. It is noteworthy, however, that even in the absence of measured changes in resistivity the electrical data for some precipitators have shown strong evidence of the suppression of back corona, a common manifestation of excessive resistivity. It is necessary, therefore, to conclude that a lowering of resistivity actually occurred in these investigations or to offer an alternative explanation for the electrical data. The discussion immediately following offers some hypotheses about the circumstances under which a lowering of high resistivity may occur. The discussion under the subsequent heading of the space-charge effect gives a different rationale for suppression of back corona (more exactly, suppression of the outward electrical manifestation of back corona).

The surface of fly ash should not, in many instances, constitute a favorable environment for the adsorption of ammonia. Moreover, the physical properties of ammonia—volatility, in particular—are such that the adsorption of the compound should not be readily accomplished under typical flue-gas conditions: a very low partial pressure of ammonia (of the order of 10 ppm) and a reasonably high temperature (around 150°C). Under what circumstances, therefore, can surface conditioning of fly ash by ammonia occur?

Fly ash with acidic surface material may be receptive to the adsorption of ammonia. However, surface material with strongly acidic properties is most likely to be adsorbed sulfur trioxide. It seems improbable that the resistivity of the normal occurring adsorbed material would be measurably lowered by the additional adsorption of ammonia, which would probably have the chemical effect of converting the acid to an ammonium salt with an increased resistivity.

Fly ash with alkaline surface material should be hostile to the adsorption of ammonia, except perhaps with simultaneous adsorption of some other gas that could mask the inherent alkalinity of the original surface material. One gas that could intervene in the manner described is water vapor. Indeed, there have been reports that the effectiveness of ammonia conditioning is increased by simultaneous injection of ammonia and water vapor;[3] however, one of the anomalies in these reports is that the quantity of water vapor added would not raise the concentration of water vapor substantially from its normal level in flue gas. Other gases that could intervene to aid the adsorption of ammonia are sulfur trioxide and sulfur dioxide. Sulfur trioxide might be present at a very low concentration and thus might not be effectively adsorbed; however, with the possibility of sulfur trioxide and ammonia reacting to form a nonvolatile salt on the fly-ash surface, the effectiveness of adsorption of both gases might be enhanced. Sulfur dioxide, although always present in flue gas at much higher concentrations than sulfur trioxide, should be difficult to collect on a fly-ash surface, either alone or in combination with ammonia (ammonium sulfites are much less stable than ammonium sulfates). There is the possibility, however, that the combination of sulfur dioxide and ammonia might be rapidly oxidized to produce an ammonium sulfate as a stable product on the fly-ash surface, provided they undergo combination to form at least a small amount of sulfite as an intermediate. The rationale for this assumption is the evidence that the oxidation of sulfur dioxide to sulfur trioxide in the atmosphere is catalyzed by ammonia, with ammonium sulfate as a stable reaction product.[50]

Enhancement of the Space-Charge Component of the Electric Field

As previously indicated in this report, the space-charge effect is attributed to the reaction between injected ammonia and normally occurring sulfur trioxide in the presence of water vapor to form a fine particulate of ammonium sulfate or ammonium bisulfate. Ionization of the reaction product within an electrostatic precipitator, by means of charge transfer from gaseous ions, produces carriers of electricity that are less mobile on the average than the carriers otherwise present. As a consequence, a higher voltage is required in the precipitator to maintain a given current density. Insofar as the collection of fly-ash particles is concerned, the benefit derived from the space-charge effect is a higher electric field in the interelectrode space for charging the fly ash and driving the particles to the collection electrodes.

The occurrence of the space-charge effect was supported experimentally by several types of observations:

- Rapid electrical changes in the precipitator as ammonia injection was either started or stopped
- Rapid appearance of fine particulate (median size by number of the order of 0.05 μm) as ammonia injection was started or disappearance of the material as injection was discontinued
- Absence of significant concentrations of ammonia in the gas phase
- Presence of ammonia as a constituent of particulate samples collected on filters and the precipitator hoppers
- Loss of sulfur trioxide from the flue gas during ammonia injection

Each of these observations, with one exception, was observed in all of the power plants using ammonia conditioning. The one exception was that involving detection of the appearance and disappearance of fine particulate by means of condensation-nuclei counting. This experimental technique was not employed in the first power-plant study, which was conducted with low-sulfur coal at the Widows Creek plant. There is no reason, however, for suspecting that the use of this experimental method would have failed to yield information similar to that found elsewhere.

In each of the power-plant studies conducted with ammonia conditioning, the flue-gas environment was conducive to the occurrence of the space-charge effect. Specifically, adequate concentrations of sulfur trioxide were present as a result of fuel combustion, and flue-gas temperatures were in a range suitable for the sulfur trioxide to react with the injected ammonia. In addition, the resistivity of the fly ash was not excessive, lying in the range from about 3×10^8 to 3×10^{11} ohm cm. Thus, the precipitators were able to operate at acceptable current densities without excessive sparking, except in the instance of the Bull Run plant, even with the added voltage drop imposed with ammonia conditioning. (Reasons for the exceptionable behavior at the Bull Run plant have been attributed in previous discussion to the probability of electrode misalignment.)

The necessary conditions for the space-charge effect were satisfied in all of the studies even though coals ranging from about 1% to 4% in sulfur content were burned as fuels. The availability of sufficient naturally-produced sulfur trioxide, despite the range in sulfur concentrations in the coals, apparently can be attributed to the chemical compositions of the fly ash. The compositions of the ash from the low sulfur coals are to be noted especially; they were low enough in alkaline components to prevent removal of sulfur trioxide from the flue gas and, thus, they were able to allow enough of this compound to remain in the gas phase to undergo reaction with the injected ammonia.

Increasing the Cohesiveness of Fly-Ash Particles

The clearest evidence of this effect was obtained at the Gallatin plant, where high-sulfur coal was used as the fuel and the fly-ash resistivity was low (about 3×10^8 ohm cm). It was apparent that ammonia conditioning was effective in overcoming loss of collected fly ash by rapping reentrainment, a problem expected to be more severe with low-resistivity ash than with high-resistivity ash. With low-resistivity ash, the electric field in the deposited ash may be insufficient to prevent reentrainment and it may even produce a positive force to intensify reentrainment;[46] with this material, therefore, the action of surface effects between particles to maintain the physical integrity of aggregates on the collection electrodes of a precipitator may be needed. With high-resistivity ash, the electric field may provide the only restraint needed to prevent reentrainment.

The exact nature of the process by which ammonia conditioning increases the cohesiveness of fly ash has not been identified. It is assumed, however, to involve a chemical reaction between the injected ammonia and the naturally occurring sulfur trioxide. Of the two possible products, ammonium sulfate and ammonium bisulfate, the latter compound can more reasonably be expected to increase cohesiveness because of its occurrence as a liquid at temperatures below 144°C.[28]

DELETERIOUS EFFECTS OF AMMONIA CONDITIONING

Enhancement of Sparking

This difficulty was encountered at the Bull Run plant during ammonia conditioning and was assumed to be a manifestation of the space-charge effect. Under the particular circumstances of this plant, however, the enhancement of sparking was attributed to electrode misalignment and possibly to poor power-supply response. With the fly ash having only a moderately high resistivity, the problem would not have been expected otherwise.

The difficulty of enhanced sparking may, however, be serious in power plants with well-aligned precipitator electrodes if the resistivity of the fly ash is normally high and not lowered by ammonia injection. In particular, the problem may be quite serious in power plants burning low-sulfur Western coals. In such plants, the net effect of ammonia injection may be deleterious unless the conditioning agent lowers the resistivity of the ash as well as creating the space-charge effect. Further research is needed to assess the net effect of ammonia conditioning under the circumstances indicated.

Increase of Fine-Particle Emission

In view of the present concern about the emission from electrostatic precipitators of fine particles (smaller than 1 or 2 μm in effective diameter), the generation of fine particles by ammonia injection would appear to be an objectionable aspect of this conditioning process. However, there are at least two observations that tend to minimize concern about the atmospheric impact of fine-particle generation. One observation is that a significant fraction of the particulate produced by ammonia conditioning is removed in a precipitator. Another observation is that a large part of the sulfur trioxide present in flue gas is converted to a collectible particulate; this means that the concentration of sulfur trioxide that can appear in the plume is lowered and that the concentration of sulfuric acid mist formed by condensation in the plume is lowered. The net result, therefore, may be an effective reduction of fine particles in the plume when ammonia conditioning is employed. Further research is needed to clarify this matter.

SECTION IX

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SECTION X

APPENDIX. EXPERIMENTAL METHODS

ANALYSIS OF COAL

Samples of coal were analyzed systematically for sulfur and ash contents by procedures included in ASTM Method D-271. Some of the samples were also analyzed for moisture and heat value by other procedures in this Method.

DETERMINATION OF THE ELECTRICAL RESISTIVITY OF FLY ASH

All of the data on the electrical resistivity of fly ash presented in this report were obtained by collecting fly ash at the inlets of electrostatic precipitators and measuring the resistivity with the samples *in situ*. Three different devices were used for this purpose. Two that were employed only in some of the initial studies of sulfur trioxide conditioning were of the cyclone type. The third device, which later became the standard apparatus for determining resistivity, was of the point-plane type.

Cyclone Resistivity Probes

Apparatus Developed by Cohen and Dickinson[26]—

The essential features of this apparatus are shown in Figure 21. Furthermore, the details of the operating procedure are given in the publication by Cohen and Dickinson.[26] The principal steps in the operation of this apparatus, however, are summarized below:

1. The assembly shown in the figure is placed near the flue-gas duct at the inlet of a precipitator and brought to the same temperature as the flue gas.
2. A stream of flue gas is pumped from the duct to the cyclone, where fly ash is deposited under centrifugal force.
3. The contents of the cyclone are rapped into the resistivity cell, which consists of two concentric cylindrical electrodes.

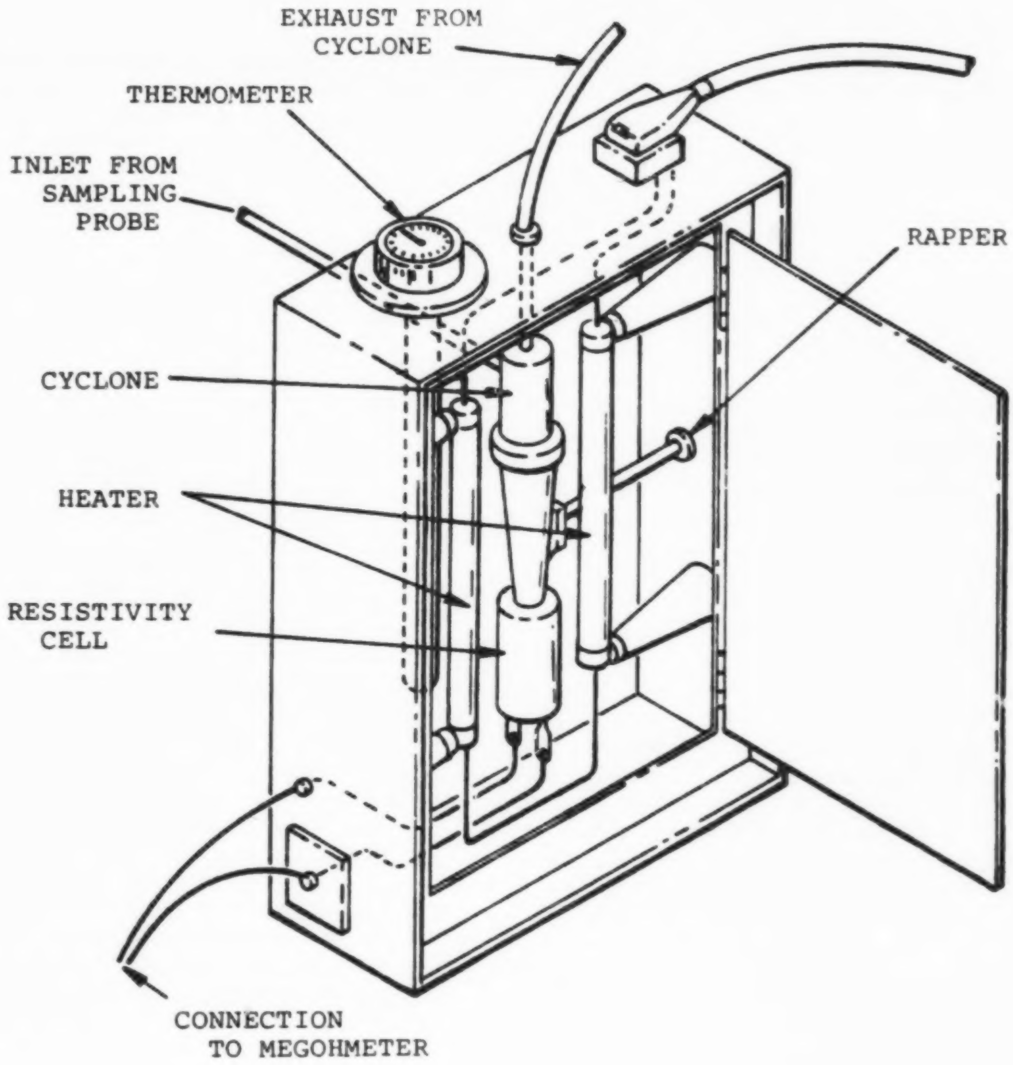
EXHAUST FROM CYCLONE
THERMOMETER
INLET FROM SAMPLING PROBE
RAPPER
CYCLONE
HEATER
RESISTIVITY CELL
CONNECTION TO MEGOHMETER

Figure 21. Resistivity apparatus using a mechanical cyclone dust collector (Cohen and Dickinson[26])

4. A known voltage is applied across the fly-ash sample and the resistivity of the ash is calculated from the applied voltage, the measured current, and the geometrical features of the resistivity cell.

Nichols[27] has discussed various problems encountered with the use of this apparatus. One of the most serious disadvantages, which led to the use of other resistivity probes during this investigation, is ensuring a constant temperature as the fly-ash sample is withdrawn from the duct and deposited in the resistivity cell.

Apparatus Designed at Southern Research Institute[27]—

A modification of the apparatus of Cohen and Dickinson that permitted the cyclone collector and resistivity to be placed within a flue-gas duct is shown in Figure 22. This apparatus was constructed at Southern Research Institute to overcome the previously mentioned problem of temperature control with the cyclone and the cell in an external chamber. A major problem in the use of this probe, as well as the apparatus of Cohen and Dickinson, was the uncertainty in knowing whether the resistivity cell had been filled with fly ash before the determination of resistivity was made.

Point-Plane Probe[27]

A point-plane resistivity probe designed at Southern Research Institute for insertion into a flue-gas duct is illustrated in Figure 23. The primary difference in the operation of this apparatus and either of the cyclone devices was that sample collection occurred under the influence of a corona and an electric field rather than a centrifugal force. The "stationary point" illustrated in the figure served as the source of a negative corona, and a circular electrode surrounded by the "grounded ring" served as the collection electrode for fly-ash particles charged by the corona. Values of resistivity were measured in two ways: (1) by comparing the values of current with different voltages applied between the corona point and the collection electrode, before and after ash was collected, and (2) by moving the "shaft" to place a second circular electrode on the upper surface of the collected ash and determining the voltage-current relationship in the sample between the adjustable and fixed electrodes. In each procedure, the calculation of resistivity was based on the thickness of the sample as determined by lowering the adjustable electrode the required distance to make contact with the sample.

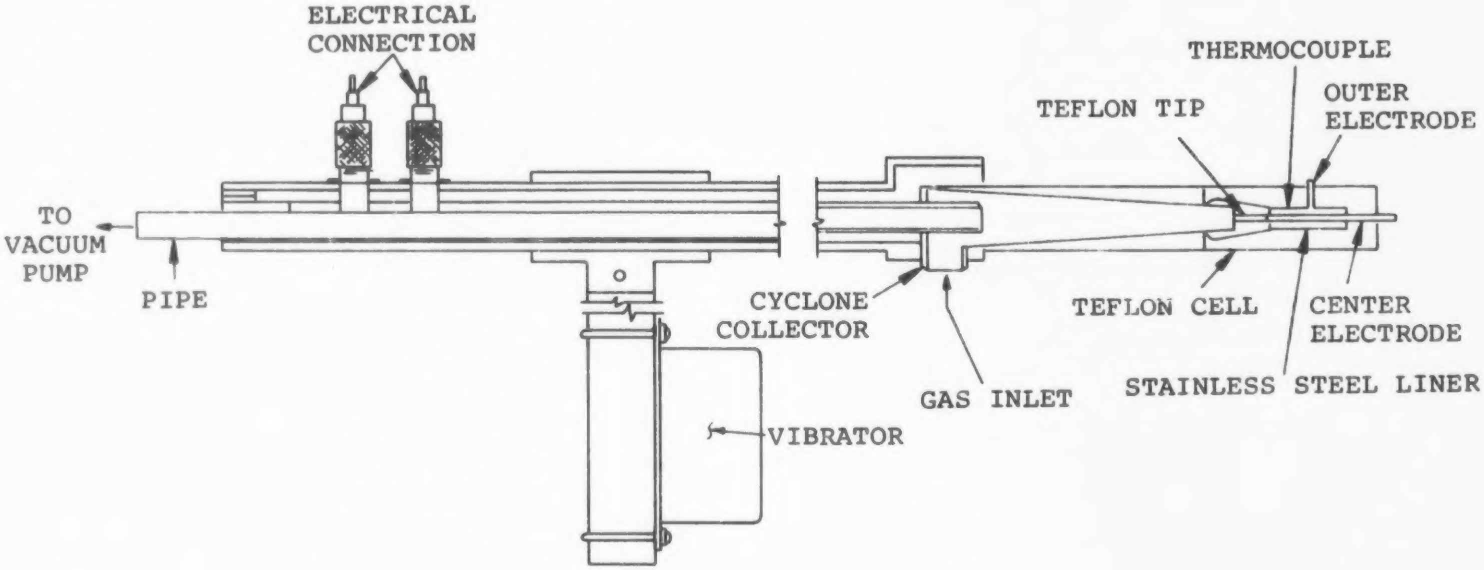
ELECTRICAL CONNECTION
THERMOCOUPLE
OUTER ELECTRODE
TEFLON TIP
TO VACUUM PUMP
PIPE
CYCLONE COLLECTOR
TEFLON CELL
CENTER ELECTRODE
GAS INLET
STAINLESS STEEL LINER
VIBRATOR

Figure 22. Cyclone probe inserted in duct (Nichols[27])

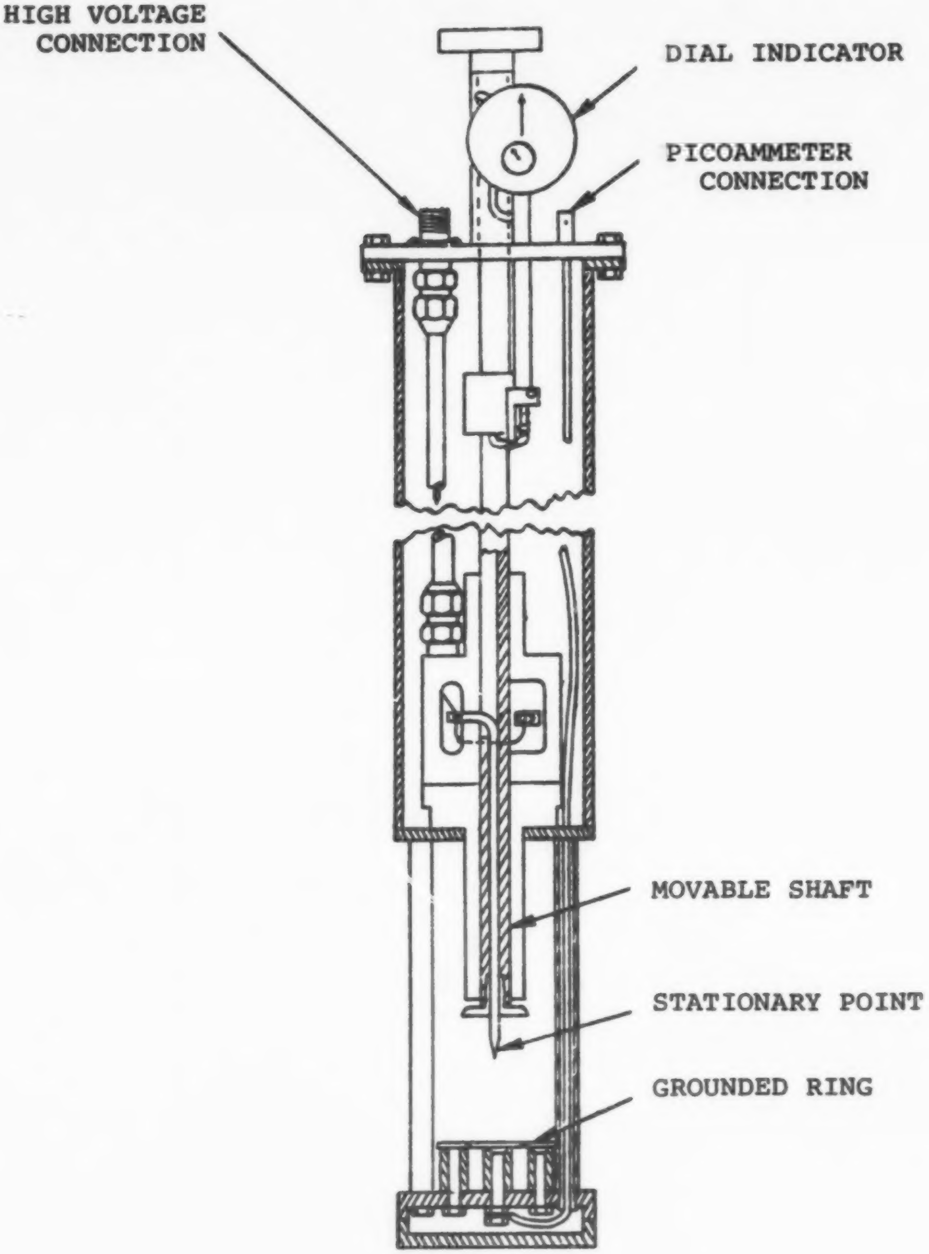
HIGH VOLTAGE CONNECTION
DIAL INDICATOR
PICOAMMETER CONNECTION
MOVABLE SHAFT
STATIONARY POINT
GROUNDED RING

Figure 23. Point-to-plane resistivity probe equipped for thickness measurement (Nichols[27])

ANALYSIS OF FLY ASH

Overall Composition

The overall composition of a sample of fly ash was determined as follows:

- One portion of the sample was dissolved in a concentrated mixture of hydrofluoric and sulfuric acids. The resulting solution was then analyzed by atomic adsorption spectroscopy for lithium, sodium, potassium, magnesium, calcium, iron, and titanium. A separate portion of the solution was analyzed colorimetrically for phosphorus.
- A second portion of the sample was fused with sodium hydroxide. The fused mixture was then dissolved in water and analyzed colorimetrically for aluminum and silicon.
- A third portion was fused with sodium carbonate. Sulfur was determined turbidimetrically as sulfate in an aqueous solution of the fused sample.

Weight percentages of the stable oxides in the original fly ash were then calculated from the concentrations of the several elements.

Water-Soluble Components

A slurry was prepared of each fly-ash sample, consisting of 0.1 g of fly ash and 30 ml of distilled water. The slurry was stirred for 20 to 30 min to dissolve the soluble constituents of the ash. Then, the following steps were followed:

1. The pH of the slurry was measured with a glass electrode to determine whether soluble acid or soluble base was in excess.
2. A portion of the liquid phase was treated with a cation-exchange resin to replace interfering cations with hydrogen ion. The sulfate in the treated liquid was then titrated with barium perchlorate to the end point indicated by Thorin. (This procedure was based on analytical methods for sulfate described by Fritz and Yamamura[51] and Fielder and Morgan.[52]
3. Another portion of the liquid was treated with sodium hydroxide, and the concentration of ammonia was determined with a membrane electrode (Model 95-10 of Orion Research Incorporated).

DETERMINATION OF FLUE GASES

Sulfur Oxides

Sulfur oxides were collected in a gas-sampling train consisting of (1) a heated sampling probe with a quartz-wool filter (to remove fly-ash particles), (2) a condenser maintained at about 80°C to collect sulfur trioxide as sulfuric acid, (3) a bubbler containing aqueous hydrogen peroxide to collect sulfur dioxide as sulfuric acid, (4) a Drierite tube to remove water vapor, and (5) a flow meter to determine the total volume of gas sampled in the dry state. The collected sulfur oxides were titrated with barium perchlorate by the precedure used for titrating soluble sulfate in fly ash. Further details on the analytical method are given in a previous report from Southern Research Institute[22] and by other investigators[43] whose design of the sulfur trioxide condenser was adopted. With the result of an independent determination of water vapor, as described below, concentrations of the sulfur oxides were calculated for the moist flue gas as sampled.

Ammonia

Ammonia was sampled through the heated sampling probe mentioned above and absorbed in a bubbler of dilute sulfuric acid. The bubbler solution was then made alkaline with sodium hydroxide, and ammonia was determined with the Orion membrane electrode.

Water Vapor

Water vapor was collected from a measured volume of flue gas in a preweighed cartridge of Drierite and determined gravimetrically.

DETERMINATION OF FINE-PARTICLE CONCENTRATIONS

Use was made of optical, diffusional, and inertial devices for determining the concentrations of fine particles. The specific items of instrumentation employed were a General Electric condensation-nuclei counter with diffusion batteries, a Climet photoelectric particle counter, and cascade impactors of the Brink and Anderson types. Reference is made to a paper by McCain *et al.*[36] for details on the operation of these instruments.

DETERMINATION OF PRECIPITATOR ELECTRICAL PARAMETERS

Some of the precipitator electrical data described in this report were obtained from readings of the manufacturer's installed meters for primary voltage and current, secondary current, and spark rate. The remaining data—principally on secondary voltage but including auxiliary information on secondary currents—were obtained with special instrumentation installed and operated by Mr. Gerald D. Whitehead, a member of the TVA technical staff.